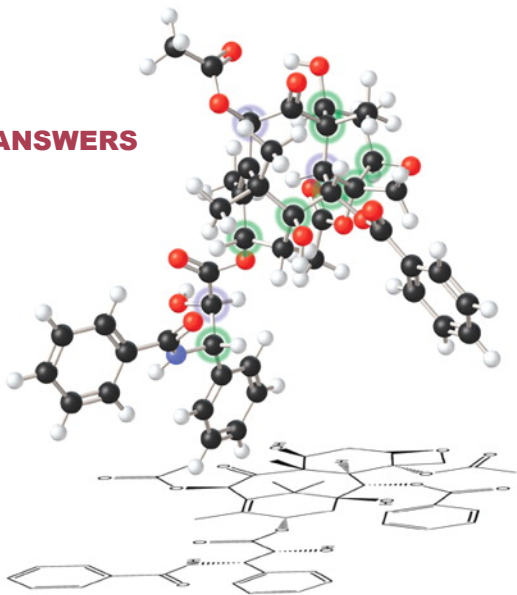


GENERAL CHEMISTRY

Principles and Modern Applications TENTH EDITION

ANSWERS



PETRUCCI

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Chapter 1 Answers

Practice Examples

1a. 177 °C

1b. -26.1 °C

2a. 1.46 g/mL

2b. 2.987 cm

3a. 2.76 g/cm³

3b. The water level will remain unchanged.

4a. 1.8 kg ethanol

4b. 0.857 g/mL

5a. 21.3

5b. 1.1×10^6

6a. 26.7

6b. 15.6

Integrative Example

A. 14%

B. 4.239×10^{23} Na atoms

Exercises

1. One theory is preferred over another if it can correctly predict a wider range of phenomena and if it has fewer assumptions.

3. For a given set of conditions, a cause, is expected to produce a certain result or effect. Although these cause-and-effect relationships may be difficult to unravel at times (“God is subtle”), they nevertheless do exist (“He is not malicious”).

5. The experiment should be carefully set up so as to create a controlled situation in which one can make careful observations after altering the experimental parameters, preferably one at a time. The results must be reproducible (to within experimental error) and, as more and more experiments are conducted, a pattern should begin to emerge, from which a comparison to the current theory can be made.

7a. Physical

7b. Chemical

7c. Chemical

7d. Physical

9a. Homogeneous mixture

9b. Heterogeneous mixture

9c. Heterogeneous mixture

9d. Substance

11a. If a magnet is drawn through the mixture, the iron filings will be attracted to the magnet and the wood will be left behind.

11b. When the glass-sucrose mixture is mixed with water, the sucrose will dissolve, whereas the glass will not. The water can then be boiled off to produce pure sucrose.

11c. Olive oil will float to the top of a container and can be separated from water, which is more dense. It would be best to use something with a narrow opening that has the ability to drain off the water layer at the bottom (i.e., buret).

11d. The gold flakes will settle to the bottom if the mixture is left undisturbed. The water then can be decanted (i.e., carefully poured off).

13a. 8.950×10^3

13b. 1.0700×10^4

13c. 2.40×10^{-2}

13d. 4.7×10^{-3}

13e. 9.383×10^2

13f. 2.75482×10^5

15a. 3.4×10^4 cm/s

15b. 6.378×10^3 km

15c. 7.4×10^{-11} m

15d. 4.6×10^5

17a. exact number

17b. measured quantity

17c. measured quantity

17d. measured quantity

- 19a. 3985
- 19b. 422.0
- 19c. 1.860×10^5
- 19d. 3.390×10^4
- 19e. 6.321×10^4
- 19f. 5.047×10^{-4}
- 21a. 9.3×10^{-4}
- 21b. 2.2×10^{-1}
- 21c. 5.4×10^{-1}
- 21d. 3.058×10^1
- 23a. 2.44×10^4
- 23b. 1.5×10^3
- 23c. 40.0
- 21d. 2.131×10^3
- 21e. 4.8×10^{-3}
- 25a. 186.30 km/h
- 25b. 9.95 km/kg
- 27a. 127 mL
- 27b. 0.0158 L
- 27c. 0.981 L
- 27d. $2.65 \times 10^6 \text{ cm}^3$
- 29a. 174 cm
- 29b. 29 m
- 29c. 644 g
- 29d. 112 kg
- 29e. 7.00 dm^3

- 29f. 3.52×10^3 mL
31. $3245 \mu\text{g}$
33. 1.5 m
- 35a. 10. s
- 35b. 9.83 m/s
- 35c. 2.5 min
37. 2.47 acres
39. $2.2 \times 10^3 \text{ g/cm}^2$, $2.2 \times 10^4 \text{ kg/m}^2$
41. Low: 14°F , high: 122°F
43. A temperature of -465°F cannot be achieved because it is below absolute zero.
- 45a. 35.1°M
- 45b. -59.2°M
47. 0.958 g/mL
49. 0.790 g/mL
51. 0.629 kg acetone
53. 1.07 kg fertilizer
55. $1.04 \times 10^4 \text{ g}$ iron
57. iron bar < aluminum foil < water
59. $1.82 \times 10^{-2} \text{ mm}$
61. 0.9 L blood
63. 9.2% A, 28.9% B, 48.7% C, 11% D, 3% F
65. $1.10 \times 10^3 \text{ g}$ sucrose

Integrative and Advanced Exercises

71. 5.4×10^{16} tons
72. 38.8 m

74a. $\frac{5 \text{ mg}}{1\text{m}^2 \cdot 1\text{h}}$

74b. $4.1 \times 10^5 \text{ h}$

76a. $-101.\underline{25} \text{ }^\circ\text{C}$

76b. $160. \text{ }^\circ\text{C}$

76c. $-19.1 \text{ }^\circ\text{C}$

76d. $335 \text{ }^\circ\text{C}$

80. 11 g/mL

81. $1.98 \times 10^4 \text{ kg}$ sodium hypochlorite

84. 0.25 g/cm^3

85a. 0.867 g/cm^3

85b. 1.02 g/cm^3

85c. 0.869 g/cm^3

85d. $\%N = 58.4$

86. 76.4 m

87. 347.3 g ethanol

88. 0.119 mm

89. 2.1 glasses of wine

Feature Problems

94. The information provided in sketches (a) and (d) allows calculation of the density. Density of the plastic material = $1.12 \frac{\text{g}}{\text{cm}^3}$.

Self-Assessment Exercises

99. The answer is (e), a natural law.

100. The answer is (a).

101. The answer is (c).

102. The answer is (d) and (f).

103. The answer is (d).
104. The answer is (b).
107. The answer is (b).
108. (e), (a), (c), (b), (d), listed in order of increasing significant figures.
109. The answer is (d).
110. 0.114 mm
111. No.

Chapter 2 Answers

Practice Examples

1a. 0.529 g magnesium nitride

1b. 6.85 g magnesium

2a. 1.20 g Mg , 0.80 g oxygen.

2b. 16.61 g of MgO (product) and 3.39 g of unreacted O₂ .

3a. $^{109}_{47}\text{Ag}$

3b. $^{116}_{50}\text{Sn}^{2+}$, $^{117}_{50}\text{Sn}^{2+}$, $^{118}_{50}\text{Sn}^{2+}$, $^{119}_{50}\text{Sn}^{2+}$, and $^{120}_{50}\text{Sn}^{2+}$ are all possible answers.

4a. 16.830885

4b. $^{158}_{64}\text{Gd}$, 157.9241 u, 9.87340 .

5a. Boron-11

5b. In-115

6a. 28.08 u

6b. 7.5% lithium - 6, 92.5% lithium - 7

7a. Li⁺ , S²⁻ , Ra²⁺ , F⁻ , I⁻ , Al³⁺ .

7b. Na is a main-group metal in group 1(1A).

Re is a transition metal in group 7(7B).

S is a main-group nonmetal in group 16(6A)

I is a main-group nonmetal in group 17(7A).

Kr is a nonmetal in group 18(8A).

Mg is a main-group metal in group 2(2A).

U is an inner transition metal, an actinide.

Si is a main-group metalloid in group 14(4A).

B is a metalloid in group 13(3A).

Al is a main-group metal in group 13(3A).

As is a main-group metalloid in group 15(5A).

8a. 248 g Cu

8b. 1.58×10^{22} ^{206}Pb atoms

9a. 3.46×10^{21} Pb atoms

9b. 62.5%

Integrative Example

A. 9.14×10^5 atoms of ^{63}Cu

B. 2.4477×10^6 servings, No.

Exercises

1. The observations cited do not necessarily violate the law of conservation of mass. The oxide formed when iron rusts is a solid and remains with the solid iron, increasing the mass of the solid by an amount equal to the mass of the oxygen that has combined. The oxide formed when a match burns is a gas and will not remain with the solid product (the ash); the mass of the ash thus is less than that of the match. We would have to collect all reactants and all products and weigh them to determine if the law of conservation of mass is obeyed or violated.

3. 0.268 g oxygen

5. Compare the mass before reaction (initial) with that after reaction (final). These data support the law of conservation of mass.

7a. 0.397

7b. 0.659

7c. 60.3%

9. The two samples of sodium chloride have the same %Na.

11. 0.422 g sulfur

13. For a given mass of sulfur, the mass of oxygen in the second compound (SO_3) relative to the mass of oxygen in the first compound (SO_2) is in a ratio of 3:2. These results are entirely consistent with the Law of Multiple Proportions because the same two elements, sulfur and oxygen in this case, have reacted together to give two different compounds that have masses of oxygen that are in the ratio of small positive integers for a fixed amount of sulfur.

15a. These results are consistent with the Law of Multiple Proportions because the masses of hydrogen in the three compounds end up in a ratio of small whole numbers when the mass of nitrogen in all three compounds is normalized to a simple value (1.000 g here).

15b. Compound A might be N_2H_6 and compound C, N_2H_4 .

17. $\approx 11\%$

19. Calculate the charge on each drop, express each in terms of 10^{-19} C. Finally, express each in terms of $e = 1.6 \times 10^{-19}$ C. The values are consistent with the charge that Millikan found for that of the electron, and he could have inferred the correct charge from these data, since they are all multiples of e .

21a. Determine the ratio of the mass of a hydrogen atom to that of an electron. Use the mass of a proton plus that of an electron for the mass of a hydrogen atom.

21b. Use data in Table 2-1 to compare the mass-to-charge ratios those for the proton (a hydrogen ion, H^+) and the electron. The hydrogen ion is the lightest positive ion available. The mass-to-charge ratio for a positive particle is considerably larger than that for an electron.

23a. ${}^{60}_{27}\text{Co}$

23b. ${}^{32}_{15}\text{P}$

23c. ${}^{59}_{26}\text{Fe}$

23d. ${}^{226}_{88}\text{Ra}$

25.	Name	Symbol	number of protons	number of electrons	number of neutrons	mass number
	sodium	${}^{23}_{11}\text{Na}$	11	11	12	23
	silicon	${}^{28}_{14}\text{Si}$	14	14^a	14	28
	rubidium	${}^{85}_{37}\text{Rb}$	37	37^a	48	85
	potassium	${}^{40}_{19}\text{K}$	19	19	21	40
	arsenic ^a	${}^{75}_{33}\text{As}$	33^a	33	42	75
	neon	${}^{20}_{10}\text{Ne}^{2+}$	10	8	10	20
	bromine ^b	${}^{80}_{35}\text{Br}$	35	35	45	80
	lead ^b	${}^{208}_{82}\text{Pb}$	82	82	126	208

^a This result assumes that a neutral atom is involved.

^b Insufficient data. Does not characterize a specific nuclide; several possibilities exist. The minimum information needed is the atomic number (or some way to obtain it, such as from the name or the symbol of the element involved), the number of electrons (or some way to obtain it, such as the charge on the species), and the mass number (or the number of neutrons).

27a. 46 protons, 46 electrons, 62 neutrons

27b. 8.9919908

29. 106.936 u

31a. 2.914071

31b. 2.165216

31c. 18.50146

33a. $^{35}_{17}\text{Cl}^{-}$

33b. $^{60}_{27}\text{Co}^{3+}$

33c. $^{124}_{50}\text{Sn}^{2+}$

35. calcium

37. 53 protons, 54 electrons, 70 neutrons.

39. 95 protons, 95 electrons, 146 neutrons.

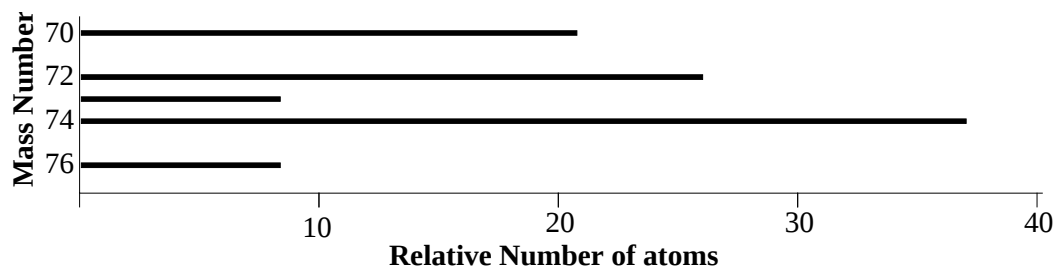
41. There are no chlorine atoms that have a mass of 35.4527 u.

43. 24.31 u

45. 108.9 u

47. 40.962 u

49a.



49b. Average atomic mass of germanium = 72.6. The result is only approximately correct because the isotopic masses are given to only two significant figures.

51a. Ge

51b. Other elements in group 16(6A) are similar to S: O, Se, and Te. Most of the elements in the periodic table are unlike S, but particularly metals such as Na, K, and Rb.

51c. Rb

51d. At

53a. 118

53b. 119

55a. 9.51×10^{24} atoms Fe

55b. 2.81×10^{20} atoms Ag

55c. 5.1×10^{13} atoms Na

57a. 6.347 mol Zn

57b. 1.707×10^{27} atoms Cr

57c. 3.3×10^{-10} g Au

57d. $\frac{3.154760 \times 10^{-23} \text{ g F}}{1 \text{ atom F}}$

59. 2.4×10^{22} Cu atoms

61. 8.7×10^{18} atoms ^{204}Pb

63a. 1.45×10^{-6} mol Pb / L

63b. 8.7×10^{14} Pb atoms / mL

65. Answer (b).

Integrative and Advanced Exercises

70. $3 \times 10^{15} \text{ g/cm}^3$

72a. ^{234}Th

72b. Ti^{2+} . There is not enough information to determine the mass number.

72c. $^{110}\text{Sn}^{2+}$

74. ^{210}Po

76. 0.36%

77. 200.6 u

82. 2.3×10^{21} Si atoms

86. 50.1% Sn, 32.0% Pb, 17.9% Cd.

87. 102 cm^3

Feature Problems

89. The sensitivity of Lavoisier's balance can be as little as 0.01 grain, which seems to be the limit of the readability of the balance; alternatively, it can be as large as 3.12 grains, which assumes that all of the error in the experiment is due to the (in)sensitivity of the balance. Convert 0.01 grains and 3.12 grains to grams. Lavoisier's results conform closely to the law of conservation of mass. The difference between reactant mass and product mass (in grams) falls between the maximum error of a common modern laboratory balance and the minimum error of a good quality analytical balance.

92. $2.43 \times 10^5 \text{ km}^3$

93. 159 ppm Rb

Self-Assessment Exercises

97. The answer is (b).

98. The answer is (d).

99. The answer is (c).

100. The answer is (a).

101. The answer is (d).

102. ${}_{17}^{35}\text{Cl}^+$

103. The answer is (d).

104a. Group 18

104b. Group 17

104c. Group 13 and Group 1

104d. Group 18

105. (d) and (f)

106. The answer is (c).

107. The answer is (d).

108. The answer is (b).

109. Fe_2O_3 and Fe_3O_4

110. $^{86}\text{Sr} = 9.5\%$, $^{87}\text{Sr} = 7.3\%$. The reason for the imprecision is the low number of significant figures for ^{84}Sr .

111. 1.2×10^{14} atoms of Au

Chapter 3 Answers

Practice Examples

1a. 4.0×10^1 g MgCl_2

1b. 8.12×10^{15} NO_3^- ions, 2.44×10^{16} O

2a. 3.69×10^{21} Au atoms

2b. The vapor will be detectable.

3a. 18.9 g Br

3b. 175 mL $\text{C}_2\text{HBrClF}_3$

4a. 23.681% C, 3.180% H, 13.81% N, 18.32% P, 41.008% O.

4b. Both (b) and (e) have the same empirical formula, that is, CH_2O . These two molecules have the same percent oxygen by mass.

5a. The empirical formula of the compound is $\text{C}_3\text{H}_7\text{O}_3$. The molecular formula is $\text{C}_6\text{H}_{14}\text{O}_6$.

5b. The empirical formula of the compound is $\text{C}_{13}\text{H}_{16}\text{O}_8\text{Cl}_{12}$. The molecular formula is $\text{C}_{13}\text{H}_{16}\text{O}_8\text{Cl}_{12}$.

6a. $\text{C}_7\text{H}_{14}\text{O}_2$

6b. $\text{C}_4\text{H}_4\text{S}$

7a. For an atom of a free element, the oxidation state is 0; each Cr has an O.S. = +6; each chlorine has an O.S. = +1; each oxygen has an O.S. = $-1/2$.

7b. Each S has an O.S. = +2; each Hg has O.S. = +1; the O.S. of Mn is +7; , the O.S. of C is 0.

8a. Li_2O , SnF_2 , Li_3N .

8b. Al_2S_3 , Mg_3N_2 , V_2O_3 .

9a. cesium iodide, calcium fluoride, iron(II) oxide, chromium (III) chloride.

9b. calcium hydride, copper(I) chloride, silver(I) sulfide, mercury(I) chloride.

10a. sulfur hexafluoride, nitrous acid, calcium bicarbonate or calcium hydrogen carbonate, iron(II) sulfate.

10b. ammonium nitrate, phosphorus trichloride, hypobromous acid, silver(I) perchlorate, iron(III) sulfate.

11a. BF_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , CaCl_2 .

11b. $\text{Al}(\text{NO}_3)_3$, P_4O_{10} , $\text{Cr}(\text{OH})_3$, HIO_3 .

12a. (a) Not isomers; (b) Molecules are isomers.

12b. (a) Molecules are isomers; (b) Not isomers.

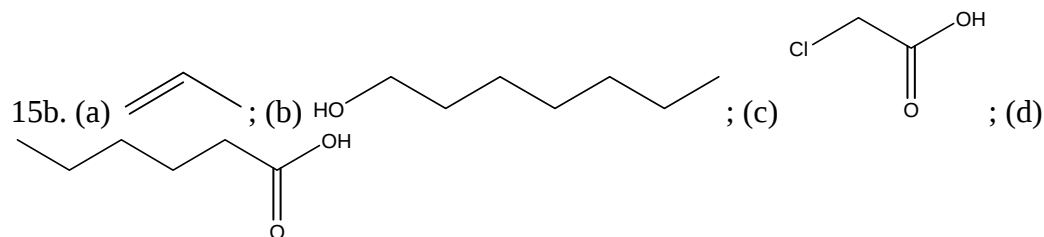
13a. (a) alkane; (b) chloroalkane; (c) carboxylic acid; (d) alkene.

13b. (a) alcohol; (b) carboxylic acid; (c) chloro carboxylic acid; (d) bromoalkene.

14a. (a) 2-propanol; (b) 1-iodopropane; (c) 3-methylbutanoic acid; (d) propene.

14b. (a) 2-chloropropane; (b) 1,4-dichlorobutane; (c) 2-methyl propanoic acid.

15a. (a) $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$; (b) $\text{CH}_3\text{CO}_2\text{H}$; (c) $\text{ICH}_2(\text{CH}_2)_6\text{CH}_3$; (d) $\text{CH}_2(\text{OH})(\text{CH}_2)_3\text{CH}_3$.



Integrative Examples

A. The compound is magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$. The compound is $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$.

B. The compound is $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The oxidation state of Cu is +2 and Cl is +7.

Exercises

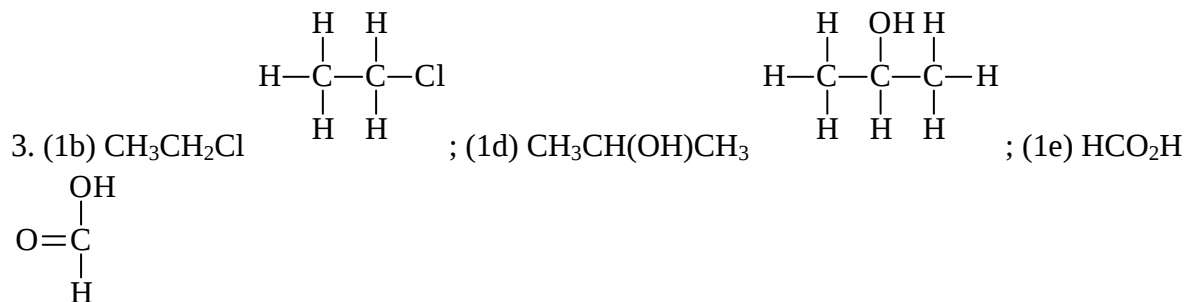
1a. H_2O_2

1b. $\text{CH}_3\text{CH}_2\text{Cl}$

1c. P_4O_{10}

1d. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

1e. HCO_2H



5a. 21 atoms

5b. 1.29×10^{22} atoms

5c. 2.195×10^{25} F atoms

7a. 149.213 u / $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$ molecule

7b. There are 11 moles of H atoms in each mole of $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$ molecules.

7c. 60.055 g C

7d. 2.73×10^{25} C atoms

9. The greatest number of N atoms is present in 50.0 g N_2O , answer (a).

11a. 1.25 mol N_2O_4

11b. 0.587 mol N atoms

11c. 0.206 mol N atoms

13. 3×10^{22} Fe atoms

15a. False

15b. True

15c. False

15d. False

17a. 41 atoms

17b. 0.800 H atoms/O atom

17c. 1.026

17d. Uranium

17e. 15.1 g of $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

19. 15.585% H

21. 15.88 %H

23. 74.046% C , 7.4566% H , 8.6349% N , 9.8634% O .

25a. 64.06 % Pb

25b. 45.497 % Fe

25c. 2.7202 % Mg

27. Oxide with the largest %Cr will have the largest number of moles of Cr per mole of oxygen.
Arranged in order of increasing %Cr: $\text{CrO}_3 < \text{CrO}_2 < \text{Cr}_2\text{O}_3 < \text{CrO}$.

29. SO_3 (40.05% S) and S_2O (80.0 % S).

31. $\text{C}_4\text{H}_{10}\text{O}_3$

33a. $\text{C}_{19}\text{H}_{16}\text{O}_4$

33b. $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2\text{S}_2$

35. $\text{C}_{14}\text{H}_{10}$

37. $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$

39. titanium

41. 894 u

43a. 90.49 % C , 9.495 % H .

43b. C_4H_5

43c. C_8H_{10}

45. CH_4N

47. C_{10}H_8 . The compound with the largest number of moles of C per mole of the compound will produce the largest amount of CO_2 and, thus, also the largest mass of CO_2 .

49. 3.710 g CO_2 , 1.898 g H_2O .

51a. $C = -4$ in CH_4

51b. $S = +4$ in SF_4

51c. $O = -1$ in Na_2O_2

51d. $C = 0$ in $C_2H_3O_2^-$

51e. $Fe = +6$ in FeO_4^{2-}

53. Cr_2O_3 , CrO_2 , CrO_3

55a. $O = +2$ in OF_2

55b. $O = +1$ in O_2F_2

55c. $O = \frac{-1}{2}$ in CsO_2

55d. $O = -1$ in BaO_2

57a. strontium oxide

57b. zinc sulfide

57c. potassium chromate

57d. cesium sulfate

57e. chromium(III) oxide

57f. iron(III) sulfate

57g. magnesium hydrogen carbonate or magnesium bicarbonate

57h. ammonium hydrogen phosphate

57i. calcium hydrogen sulfite

57j. copper(II) hydroxide

57k. nitric acid

57l. potassium perchlorate

57m. bromic acid

57n. phosphorous acid

59a. carbon disulfide

59b. silicon tetrafluoride

59c. chlorine pentafluoride

59d. dinitrogen pentoxide

59e. sulfur hexafluoride

59f. diiodine hexachloride

61a. $\text{Al}_2(\text{SO}_4)_3$

61b. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

61c. SiF_4

61d. Fe_2O_3

61e. C_3S_2

61f. $\text{Co}(\text{NO}_3)_2$

61g. $\text{Sr}(\text{NO}_2)_2$

61h. $\text{HBr}(\text{aq})$

61i. HIO_3

61j. PCl_2F_3

63a. TiCl_4

63b. $\text{Fe}_2(\text{SO}_4)_3$

63c. Cl_2O_7

63d. $\text{S}_2\text{O}_8^{2-}$

65a. chlorous acid

65b. sulfurous acid

65c. hydroselenic acid

65d. nitrous acid

67a. oxygen difluoride, not ionic.

67b. xenon difluoride, not ionic.

67c. copper (II) sulfite, ionic.

67d. ammonium hydrogen phosphate, ionic.

69. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

71. 22.3 g CuSO_4

73. $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$

75. Answer is (b), 2-butanol.

77. Molecules (a), (b), (c), and (d) are structural isomers.

79a. $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$

79b. $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$

79c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$

79e. $\text{CH}_3\text{CH}_2\text{F}$

81a. methanol; CH_3OH ; Molecular mass = 32.04 u.

81b. 2-chlorohexane; $\text{CH}_3(\text{CH}_2)_3\text{CHClCH}_3$; Molecular mass = 120.6 u.

81c. pentanoic acid; $\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$; Molecular mass = 102.1 u.

81d. 2-methyl-1-propanol; $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$; Molecular mass = 74.12 u.

Integrative and Advanced Exercises

83. 1.24×10^{23} Li – 6 atoms

86. An additional 2.500 kg mass is required.

89. It is not possible to have less than 1 molecule of S_8 . 426 yoctograms .

91. CH_4

93. % H_2SO_4 = 85.0 % , % H_2O = 15.0 %.

95. 0.05 ppb

96. 4.0 mg Kr

99. 26.9 g/mol

103. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

106. $\text{C}_{12}\text{H}_8\text{Cl}_6\text{O}$

110. I_2Cl_6

Feature Problems

111a. % P = 4.37% , % K = 4.15% .

111b. (i) 60.6% P_2O_5 ; (ii) 53.7% P_2O_5 .

111c. A “17.7-44.6-10.5” fertilizer.

111d. It is impossible to make a “5-10-5” fertilizer if the only fertilizing components are $(\text{NH}_4)_2\text{HPO}_4$ and KCl.

113a. $4.7 \times 10^3 \text{ m}^2$

113b. 2.5 nm

113c. 5.8×10^{23} molecules per mole of oleic acid

Self-Assessment Exercises

118. The answer is (c).

119. The answer is (b).

120. The answer is (d).

121. The answer is (a).

122. The answer is (c).

123. The answer is (c).

124. The answer is (b).

125. The answer is (d).

126. The answer is (d).

127. $\text{Na}_2\text{SO}_3 \cdot 7 \text{ H}_2\text{O}$

128a. % Cu = 57.46%

128b. 719.5 g

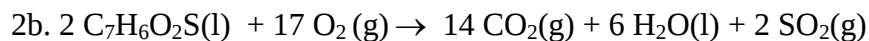
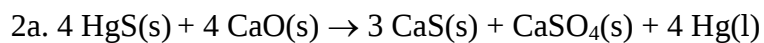
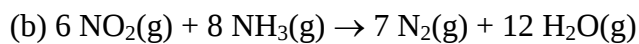
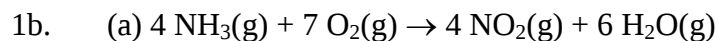
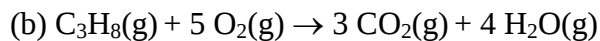
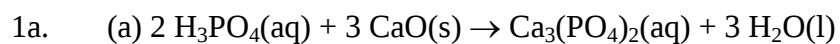
129. $\text{C}_8\text{H}_9\text{NO}_2$

130a. 75.67% C, 8.795% H, 15.45% O

130b. $\text{C}_{13}\text{H}_{18}\text{O}_2$

Chapter 4 Answers

Practice Examples



3a. 2.64 mol O_2

3b. 8.63 mol Ag

4a. 5.29 g Mg_3N_2

4b. 126 g H_2

5a. 0.710 g NH_3

5b. 3.50 g $\text{O}_2(\text{g})$

6a. 3.34cm^3 alloy

6b. 0.79 g Cu

7a. 0.4 mg $\text{H}_2(\text{g})$

7b. 0.15 g CO_2

8a. 0.307 M

8b. 0.524 M

9a. 115 g NaNO_3

9b. 50.9 g $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

10a. 0.0675 M

10b. 0.122 M

11a. 18.1 mL

11b. 4.96 g Ag_2CrO_4

12a. 936 g PCl_3

12b. 1.86 kg POCl_3

13a. 3.8 g P_4

13b. 57 g O_2 remaining

14a. (a) 30.0 g CH_2O ; (b) 25.7 g CH_2O (g); (c) 85.6 % yield .

14b. 93.7%

15a. 41.8 g CO_2

15b. 69.0 g impure $\text{C}_6\text{H}_{11}\text{OH}$

16a. 2.47×10^3 g HNO_3

16b. Approximately 56 g of SiO_2 and 30 g of KNO_3 are needed.

17a. 83 wt%

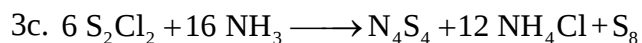
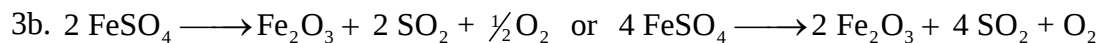
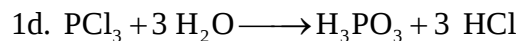
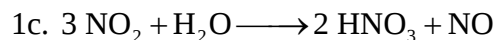
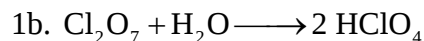
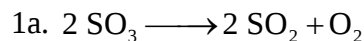
17b. 19.47%

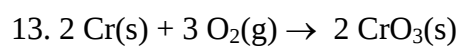
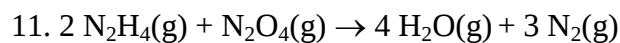
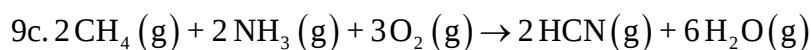
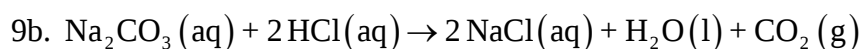
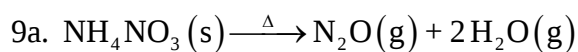
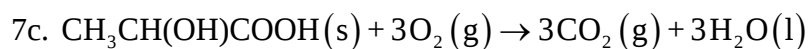
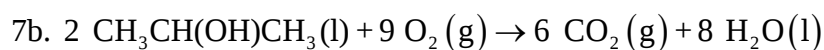
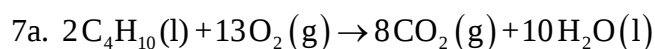
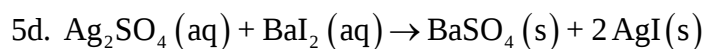
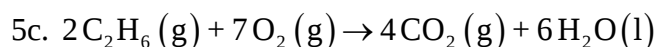
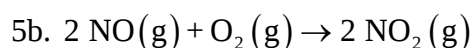
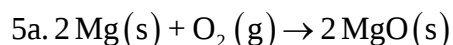
Integrative Example

A. 78.3% yield

B. 83.4 % Zn

Exercises





15. 785 g

17a. 0.402 mol O_2

17b. 128 g KClO_3

17c. 43.9 g KCl

19. 96.0 g Ag_2CO_3

21a. 12.2 g H_2

21b. 48.1 g H_2O

21c. 284 g CaH_2

23. 79.7% Fe_2O_3

25. % by mass $\text{B}_{10}\text{H}_{14} = 25.8\%$

27. 1.03g H_2

29. Al produces the largest amount of H_2 per gram of metal.

31a. 0.408 M

31b. 0.154 M

31c. 1.53 M

33a. 1.753 M

33b. 0.320 M $\text{CO}(\text{NH}_2)_2$

33c. 0.206 M

35a. 4.73g

35b. 44.1mL CH_3OH

37a. $4.7 \frac{\text{mmol C}_6\text{H}_{12}\text{O}_6}{\text{L}}$

37b. Molarity = $4.7 \times 10^{-3} \frac{\text{mol C}_6\text{H}_{12}\text{O}_6}{\text{L}}$

39. Solution (d) is a 0.500 M KCl solution.

41. The 46% by mass sucrose solution is the more concentrated.

43. 0.0820 M

45. 0.236 M

47. The ratio of the volume of the volumetric flask to that of the pipet would be 20:1. We could use a 100.0-mL flask and a 5.00-mL pipet, a 1000.0-mL flask and a 50.00-mL pipet, or a 500.0-mL flask and a 25.00-mL pipet. There are many combinations that could be used.

49a. 0.177 g Na_2S

49b. 0.562 g Ag_2S

51. 59.4mL K_2CrO_4

53. $8.46 \times 10^{-3} \frac{\text{mol HNO}_3}{\text{L}}$

55a. 0.0693 mol AlCl_3

55b. 2.91 M AlCl_3

57. 12.8 g Ag_2CrO_4

59. 0.624 g Na

61. 0.2649 M

63. 3.00 moles of NO (g)

65. HNO_3 (aq) is the limiting reactant, it will be completely consumed, leaving some Cu unreacted.

67. 143 g Na_2CS_3

69a. 10.5 g NH_3

69b. 10.1 g excess $\text{Ca}(\text{OH})_2$

71. 211.51 g CrSO_4

73a. 1.80 mol CCl_4

73b. 1.55 mol CCl_2F_2

73c. 86.1% yield

75. 87.6%

81. A main criterion for choosing a synthesis reaction is how economically it can be run. In the analysis of a compound, on the other hand, it is essential that all of the material present be detected. Therefore, a 100% yield is required; none of the material present in the sample can be lost during the analysis.

84. 1.22×10^3 g CO_2

86. 0.0386 g C_2H_6

87. 1.34 kg AgNO_3 per kg of I_2 produced.

89a. $\text{SiO}_2(\text{s}) + 2 \text{C}(\text{s}) \xrightarrow{\Delta} \text{Si}(\text{s}) + 2 \text{CO}(\text{g})$

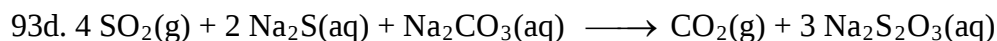
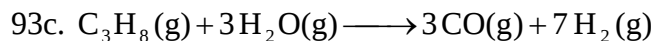
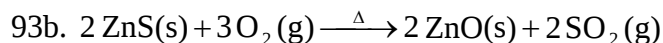
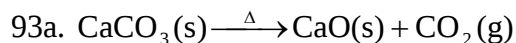
$\text{Si}(\text{s}) + 2 \text{Cl}_2(\text{g}) \rightarrow \text{SiCl}_4(\text{l})$

$\text{SiCl}_4(\text{l}) + 2 \text{H}_2(\text{g}) \rightarrow \text{Si}(\text{s, ultrapure}) + 4 \text{HCl}(\text{g})$

89b. 885 g C, 5.05×10^3 g Cl₂, 144 g H₂.

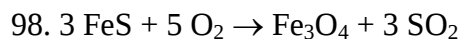
91. 73.33 %

Integrative and Advanced Exercises



95. 1.96×10^4 g LiOH

96. 68.0% CaCO₃



99. 8.88 M CH₃CH₂OH

101. 143 mL

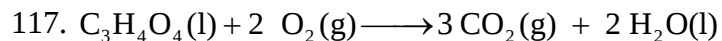
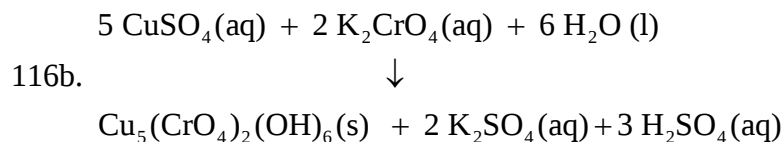
105. 0.2 cm²

106. 0.365 g Zn

114. 9.2% (C₂H₅)₂O, 90.8% CH₃CH₂OH.

115. 16.95 %

116a. Cu₅(CrO₄)₂(OH)₆



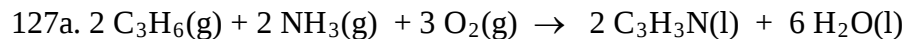
118. 5.2 g Fe, mass of excess Fe₂O₃ = 2.1 g.

119. 0.850 g AgNO₃

120. The balanced equation for the reaction is: $\text{S}_8(\text{s}) + 4 \text{Cl}_2(\text{g}) \rightarrow 4 \text{S}_2\text{Cl}_2(\text{l})$. Both “a” and “b” are consistent with the stoichiometry of this equation.

121. 1.25 g $\text{C}_3\text{N}_3(\text{OH})_3$

123. We must use all of the most concentrated solution and dilute this solution down using the next most concentrated solution. A total of 374 mL may be prepared this way.



127b. 555 kg NH_3

Self-Assessment Exercises

135. The answer is (d).

136. The answer is (d).

137. The answer is (a).

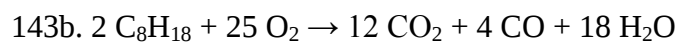
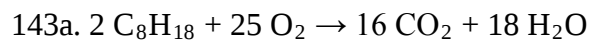
138. The answer is (a).

139. The answer is (c).

140. The answer is (d).

141. The answer is (b).

142. The answer is (d).



144. Dolomite is the compound.

145. The answer is (b).

146. The answer is (c).

Chapter 5 Answers

Practice Examples

1a. 0.540 M Cl^-

1b. (a) $7.9 \times 10^{-5} \text{ M F}^-$; (b) 3.1 kg CaF_2

2a. (a) $\text{Al}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s})$

(b) No reaction occurs.

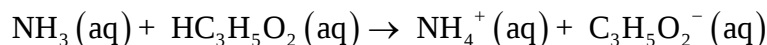
(c) $\text{Pb}^{2+}(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$

2b. (a) $\text{Al}^{3+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{AlPO}_4(\text{s})$

(b) $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$

(c) $\text{Pb}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{PbCO}_3(\text{s})$

3a. The acid and base react to form a salt solution of ammonium propionate.



3b. $\text{CaCO}_3(\text{s}) + 2 \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{Ca}^{2+}(\text{aq}) + 2 \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$

4a. (a) It is not an oxidation–reduction reaction; (b) This is an oxidation–reduction reaction.

4b. Vanadium is oxidized, manganese is reduced.

5a. *Oxidation*: $\{\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3 \text{e}^-\} \times 2$

Reduction: $\{2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})\} \times 3$

Net equation: $2 \text{Al}(\text{s}) + 6 \text{H}^+(\text{aq}) \rightarrow 2 \text{Al}^{3+}(\text{aq}) + 3 \text{H}_2(\text{g})$

5b. *Oxidation*: $2 \text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{l}) + 2 \text{e}^-$

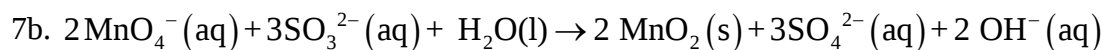
Reduction: $\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$

Net equation: $2 \text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{Br}_2(\text{l}) + 2 \text{Cl}^-(\text{aq})$

6a. $\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) + 5 \text{Fe}^{3+}(\text{aq})$

6b. $3 \text{UO}^{2+}(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 8 \text{H}^+(\text{aq}) \rightarrow 3 \text{UO}_2^{2+}(\text{aq}) + 2 \text{Cr}^{3+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$

7a. $\text{S}(\text{s}) + 2 \text{OH}^-(\text{aq}) + 2 \text{OCl}^-(\text{aq}) \rightarrow \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{Cl}^-(\text{aq})$



8a. Since the oxidation state of H is 0 in $\text{H}_2 (\text{g})$ and is +1 in both $\text{NH}_3 (\text{g})$ and $\text{H}_2\text{O} (\text{g})$, hydrogen is oxidized. A substance that is oxidized is called a reducing agent. The oxidation state of the element N decreases during this reaction, meaning that $\text{NO}_2 (\text{g})$ is reduced. The substance that is reduced is called the oxidizing agent.

8b. Au has been oxidized and, thus, $\text{Au} (\text{s})$ (oxidization state = 0), is the reducing agent. O has been reduced and thus, $\text{O}_2 (\text{g})$ (oxidation state = 0) is the oxidizing agent.

9a. 0.1019 M

9b. 0.130 M

10a. 65.4% Fe

10b. 0.03129 M

Integrative Example

A. 49.89%

B. 1.32%

Exercises

1a. Weak electrolyte

1b. Strong electrolyte

1c. Strong electrolyte

1d. Nonelectrolyte.

1e. Strong electrolyte

3. HCl is practically 100% dissociated into ions. The apparatus should light up brightly. A solution of both HCl and $\text{HC}_2\text{H}_3\text{O}_2$ will yield similar results.

5a. Barium bromide: strong electrolyte

5b. Propionic acid: weak electrolyte

5c. Ammonia: weak electrolyte

7a. 0.238 M K^+

7b. 0.334 M NO_3^-

7c. 0.166 M Al^{3+}

7d. 0.627 M Na^+

9. $3.04 \times 10^{-3} \text{ M OH}^-$

11a. $3.54 \times 10^{-4} \text{ M Ca}^{2+}$

11b. $8.39 \times 10^{-3} \text{ M K}^+$

11c. $3.44 \times 10^{-3} \text{ M Zn}^{2+}$

13. The solution containing 8.1 mg K^+ per mL gives the largest K^+ of the three solutions.

15. $4.3 \times 10^2 \text{ mg MgI}_2$

17. 0.732 M

19a. $\text{Pb}^{2+}(\text{aq}) + 2 \text{ Br}^-(\text{aq}) \rightarrow \text{PbBr}_2(\text{s})$

19b. No reaction occurs (all are spectator ions).

19c. $\text{Fe}^{3+}(\text{aq}) + 3 \text{ OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$

21a. No reaction occurs.

21b. $\text{Cu}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CuCO}_3(\text{s})$

21c. $3\text{Cu}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Cu}_3(\text{PO}_4)_2(\text{s})$

23a. Add $\text{K}_2\text{SO}_4(\text{aq})$; $\text{BaSO}_4(\text{s})$ will form and MgSO_4 will not precipitate.

23b. $\text{H}_2\text{O}(\text{l})$; $\text{Na}_2\text{CO}_3(\text{s})$ dissolves, but $\text{MgCO}_3(\text{s})$ will not dissolve (appreciably).

23c. Add $\text{KCl}(\text{aq})$; $\text{AgCl}(\text{s})$ will form, while $\text{Cu}(\text{NO}_3)_2(\text{s})$ will dissolve.

25a. $\text{Sr}(\text{NO}_3)_2(\text{aq}) + \text{K}_2\text{SO}_4(\text{aq})$: $\text{Sr}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{SrSO}_4(\text{s})$

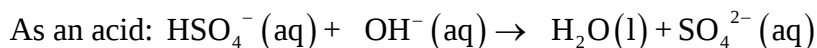
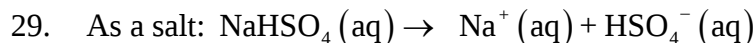
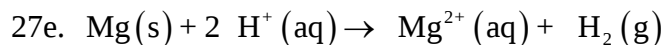
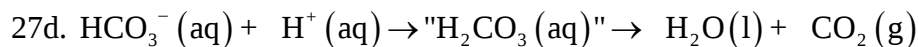
25b. $\text{Mg}(\text{NO}_3)_2(\text{aq}) + \text{NaOH}(\text{aq})$: $\text{Mg}^{2+}(\text{aq}) + 2 \text{ OH}^-(\text{aq}) \rightarrow \text{Mg}(\text{OH})_2(\text{s})$

25c. $\text{BaCl}_2(\text{aq}) + \text{K}_2\text{SO}_4(\text{aq})$: $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$

27a. $\text{OH}^-(\text{aq}) + \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$

27b. No reaction occurs. This is the physical mixing of two acids.

27c. $\text{FeS}(\text{s}) + 2 \text{ H}^+(\text{aq}) \rightarrow \text{H}_2\text{S}(\text{g}) + \text{Fe}^{2+}(\text{aq})$



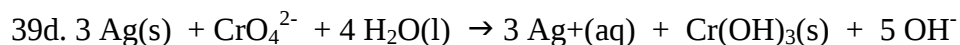
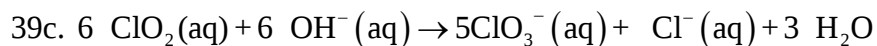
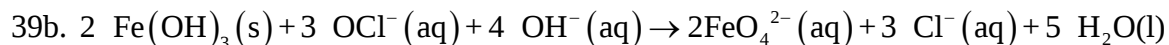
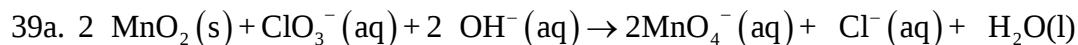
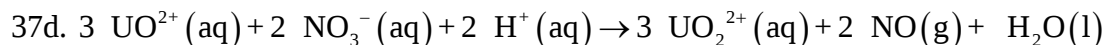
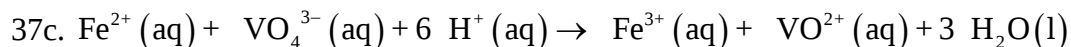
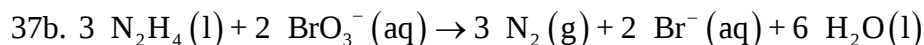
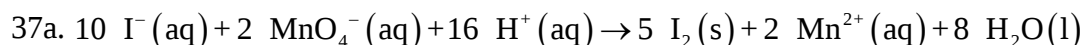
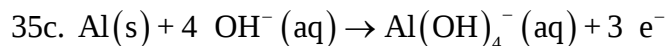
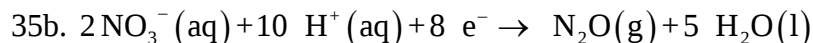
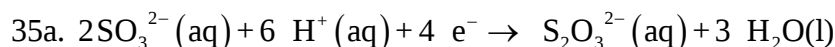
31. Use (b), $\text{NH}_3 (\text{aq})$. NH_3 affords the OH^- ions necessary to form $\text{Mg}(\text{OH})_2 (\text{s})$.

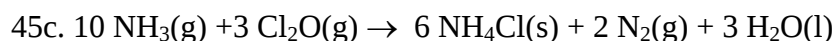
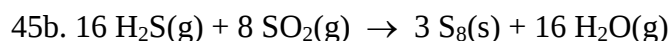
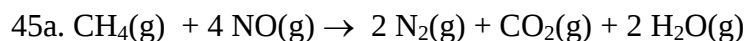
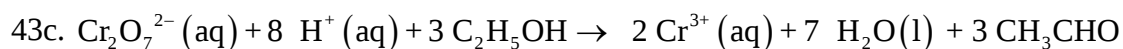
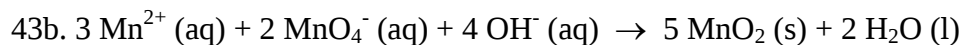
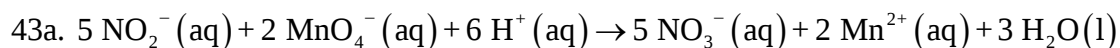
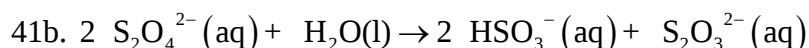
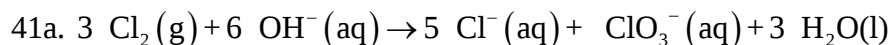
33a. The O.S. of H is +1, that of O is -2, that of C is +4, and that of Mg is +2 on each side of this equation. This is not a redox equation.

33b. The O.S. of Cl is 0 on the left and -1 on the right side of this equation. The O.S. of Br is -1 on the left and 0 on the right side of this equation. This is a redox reaction.

33c. The O.S. of Ag is 0 on the left and +1 on the right side of this equation. The O.S. of N is +5 on the left and +4 on the right side of this equation. This is a redox reaction.

33d. On both sides of the equation the O.S. of O is -2, that of Ag is +1, and that of Cr is +6. Thus, this is not a redox equation.





47a. $\text{SO}_3^{2-}(\text{aq})$ is the reducing agent; $\text{MnO}_4^-(\text{aq})$ is the oxidizing agent.

47b. $\text{H}_2(\text{g})$ is the reducing agent; $\text{NO}_2(\text{g})$ is the oxidizing agent.

47c. $[\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$ is the reducing agent; $\text{H}_2\text{O}_2(\text{aq})$ is the oxidizing agent.

49. 13.3 mL NaOH(aq) soln

51. 3.546 mL KOH solution

53. 0.1230 M NaOH

55. 0.077 M NaOH

57. Acidic

59. 34 mL base

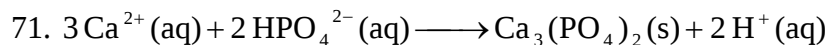
61. Answer is (d).

63. 1.968×10^{-2} M

65. 53.23% Fe

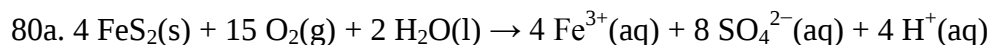
67. 37.0 g $\text{Na}_2\text{C}_2\text{O}_4$

Integrative and Advanced Exercises



74. 108 ppm Mg

75. 0.0874 L



80b. 23.4 g CaCO_3

83. 44.6 g Cl_2

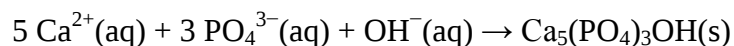
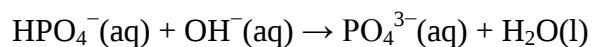
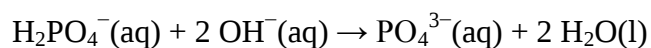
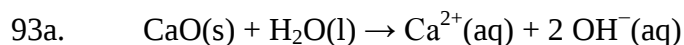
85. 5.0×10^2 g $\text{ClO}_2(\text{g})$

88a. 45.9 g

88b. 1.00 L

89. % $\text{Mg}(\text{OH})_2 = 21.6$; % $\text{Al}(\text{OH})_3 = 78.4$.

91. 0.4346 %



93b. 0.302 kg

Feature Problems

94. $x = 1.03$

95. 91.0% MnO_2

97. Before the breath test: 8×10^{-4} M; After the breath test 3×10^{-4} mol/L.

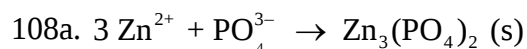
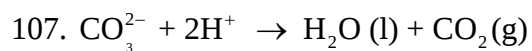
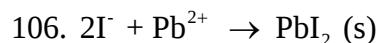
Self-Assessment Exercises

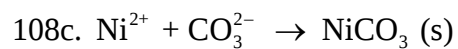
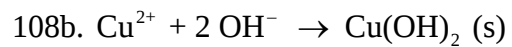
102. The answer is (b).

103. The answer is (d).

104. The answer is (c).

105. The answer is (a).





109a. Species oxidized: N in NO

109b. Species reduced: O_2

109c. Oxidizing agent: O_2

109d. Reducing agent: NO

109e. Gains electrons: O_2

109f. Loses electrons: NO

110. The answer is (b).

111. The answer is (d).

112. The answer is (a).

113a. False

113b. True

113c. False

113d. False

113e. True

114a. No

114b. Yes

114c. Yes

114d. No

Chapter 6 Answers

Practice Examples

1a. 760.mmHg

1b. 1.13 g/cm^3

2a. 756.0 mmHg

2b. 93mm glycerol

3a. 139 torr

3b. 1.35 kg. It is not necessary to add a mass with the same cross sectional area.

4a. 24.4 L NH_3

4b. 464K

5a. 2.11molHe

5b. 5.59×10^{14} molecules N_2

6a. 2.11mL

6b. 0.378 g O_2

7a. 86.4g/mol

7b. 30.0 g/mol . This answer is in good agreement with the molar mass of NO.

8a. 0.162 g/L . When compared to the density of air under the same conditions (1.16 g/L, based on the “average molar mass of air”=28.8g/mol) the density of He is only about one seventh as much. Thus, helium is less dense (“lighter”) than air.

8b. 32.0 g/mol

9a. 35.6 g NaN_3

9b. 0.619 g Na(l)

10a. 1.25 L O_2 (g)

10b. 150. L NH_3

11a. 13atm

11b. 5.5atm

12a. $0.0348 \text{ atm H}_2\text{O(g)}, 2.47 \text{ atm CO}_2\text{(g)}$.

12b. $\text{N}_2 = 584 \text{ mmHg}$, $\text{O}_2 \text{ pressure} = 157 \text{ mmHg}$, $\text{CO}_2 = 0.27 \text{ mmHg}$, $\text{Ar} = 7.0 \text{ mmHg}$.

13a. 0.00278 mol HCl

13b. 0.382 L

14a. $\text{NH}_3 \text{(g)}$, 661 m/s .

14b. 76.75 K

15a. $2.1 \times 10^{-4} \text{ mol O}_2$

15b. 28.2 s

16a. $1.90 \times 10^2 \text{ g/mol}$

16b. 52.3 s

17a. $\text{Cl}_2\text{(g)}$

17b. $\text{Cl}_2\text{(g)}$

Integrative Example

A. C_3H_4 . There are three possible Lewis structures.

B. $\text{C}_4\text{H}_9\text{NO}_3$

Exercises

1a. 0.968 atm

1b. 0.766 atm

1c. 1.17 atm

1d. 2.22 atm

3. 11.4 m benzene

5. 710 mm Hg

7. 1.03 kg cm^{-2}

9a. 52.8 L

9b. 7.27 L

11. 225 K

13. 50.6 atm

15. 255 K

17. 0.132 g Ar

19a. 41.3 mg PH_3

19b. 7.32×10^{20} molecules

21. At the higher elevation of the mountains, the atmospheric pressure is lower than at the beach. However, the bag is virtually leak proof; no gas escapes. Thus, the gas inside the bag expands in the lower pressure until the bag is filled to near bursting.

23. 4.30 L

25. 4.89 g

27. 5.32×10^4 mL

29. 702 g Kr

31. 2.1×10^{-11} Pa

33a. $24.4 \text{ L} \cdot \text{mol}^{-1}$

33b. $31.3 \text{ L} \cdot \text{mol}^{-1}$

35. 103 g/mol

37. SF_4

39. 55.8 g/mol. The formula is C_4H_8 .

41. 15.56 L/mol

43a. 1.18 g/L air

43b. The density of CO_2 is 1.80 g/L CO_2 . Since this density is greater than that of air, the balloon will not rise in air.

45. P_4

47. 378 L O_2

49. 3.1×10^7 L SO_2

51. 10.9% KClO_3
53. 73.7 L H_2
55. 5.59 L gas
57. 2.06×10^3 g Ne
59. The answer is (d).
- 61a. 842 mmHg
- 61b. $P_{\text{benzene}} = 89.5$ mmHg, $P_{\text{Ar}} = 752$ mmHg.
63. Situation (b) best represents the resulting mixture, as the volume has increased by 50%.
65. 4.0 atm
67. 2.37 L $\text{H}_2(\text{g})$
69. 751 mmHg
71. 17.9%
73. 326 m/s
75. 7.83 g/mol or 7.83 u .
77. 1.51×10^3 K
79. 6.17×10^{-21} J/molecule
81. 0.00473 mol NO_2
- 83a. 1.07
- 83b. 1.05
- 83c. 0.978
- 83d. 1.004
85. 9.80 h
- 87a. $P_{\text{ideal}} = 15.3$ atm, $P_{\text{vdw}} = 14.1$ atm, P_{ideal} is off by 1.2 atm or +8.5%.
- 87b. $P_{\text{ideal}} = 19.4$ atm, $P_{\text{vdw}} = 18.3_5$ atm, P_{ideal} is off by 1.0 atm or +5.5%.
- 87c. $P_{\text{ideal}} = 27.6$ atm, $P_{\text{vdw}} = 26.8$ atm, P_{ideal} is off by 0.8 atm or +3.0%.

89. $3.95 \times 10^7 \text{ pm}^3 / \text{He atom}$

Integrative and Advanced Exercises

94. Flask 2 $n = 0.391$, Flask 1 $n = 0.609$.

97. 2.25 atm

98. 542 L

99. 0.39 atm

101. 153 mmHg

102. 19.9% He

105. 23 L

108. $2.070 \times 10^4 \text{ L}$

109. 31 mmHg

111a. 3.42% H_2O by volume

111b. 3.42% by number

111c. 1.95 % H_2O by mass

112a. 0.40 g/L

112b. 2.9 atm

114. $\chi_{\text{O}_3} = 8.046 \times 10^{-4}$

115. 19°C

118a. 482 m/s

118b. $F_u = 1.92 \times 10^{-3}$

119. 13.6 km

121a.
$$0 = V^3 - n \left(\frac{RT + bP}{P} \right) V^2 + \left(\frac{n^2 a}{P} \right) V - \frac{n^3 ab}{P} = 0$$

121b. 7.37 L

Feature Problems

126. The atomic mass of X is 16 u which corresponds to the element oxygen. The number of atoms of X (oxygen) in each compound is : Nitryl Fluoride = 2 atoms of O, Nitrosyl Fluoride = 1 atom of O, Thionyl Fluoride = 1 atom of O, Sulfuryl Fluoride = 2 atoms of O.

127a. The $\text{N}_2(\text{g})$ extracted from liquid air has some $\text{Ar}(\text{g})$ mixed in.

127b. Because of the presence of $\text{Ar}(\text{g})$ [39.95 g/mol], the $\text{N}_2(\text{g})$ [28.01 g/mol] from liquid air will have a greater density than $\text{N}_2(\text{g})$ from nitrogen compounds.

127c. Magnesium will react with molecular nitrogen but not with Ar. Thus, magnesium reacts with all the nitrogen in the mixture, but leaves the relatively inert $\text{Ar}(\text{g})$ unreacted.

127d. The densities differ by 0.50%.

129. Just over 30 km.

Self-Assessment Exercises

133. The answer is (d).

134. The answer is (c).

135. 546 K

136. The answer is (d).

137. The answer is (b).

138. The answer is (a).

139a. False

139b. True

139c. False

139d. True

139e. False

140. The answer is (c).

141. The answer is (a).

142. The answer is (b).

143. 1.3 L of CO remain.

145. The answer is (c).

146a. Ne has higher a and b values.

146b. C_3H_8 has higher a and b values.

146c. Cl_2 has higher a and b values.

147. The height, h is inversely proportional to D . That is, the larger the diameter of the tube, the shorter the height of the liquid.

148. C_4H_{10}

149. For every single mark representing CO_2 , we need 2060 marks for N_2 , 553 marks for O_2 , and 25 for Ar.

Chapter 7 Answers

Practice Examples

1a. 32.7 kJ

1b. 4.89 kJ

2a. 3.0×10^2 g

2b. 37.9°C

3a. -3.83×10^3 kJ/mol

3b. 6.26 kJ / ° C

4a. -65. kJ/mol

4b. 33.4°C

5a. 114 J

5b. +14.6 kJ

6a. $+1.70 \times 10^2$ J

6b. 179 J of work is done by the system to the surroundings.

7a. 60.6 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

7b. 0.15 kJ heat evolved

8a. +3.31 kJ

8b. 1.72 kg H_2O

9a. -124 kJ

9b. -2006 kJ

10a. $6 \text{ C (graphite)} + \frac{13}{2} \text{ H}_2 (\text{g}) + \text{O}_2 (\text{g}) + \frac{1}{2} \text{ N}_2 (\text{g}) \rightarrow \text{C}_6\text{H}_{13}\text{O}_2\text{N (s)}$

10b. The specified reaction is twice the reverse of the formation reaction, and its enthalpy change is minus two times the enthalpy of formation of $\text{NH}_3(\text{g})$: $-2 \times (-46.11 \text{ kJ}) = +92.22 \text{ kJ}$

11a. -1367 kJ

11b. -2.5×10^3 kJ/mole of mixture

12a. -1273 kJ/mol $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$

12b. $-184 \text{ kJ/mol CH}_3\text{OCH}_3(\text{g})$

13a. $-112.3 \text{ kJ/mol AgI(s) formed}$

13b. $-505.8 \text{ kJ/mol Ag}_2\text{CO}_3(\text{s}) \text{ formed.}$

Integrative Example

A. -125.5 kJ/mol

B. The contents of the vessel after completion of the reaction are 74.1 g of Ca(OH)_2 and 66.3 g of H_2O .

Exercises

1a. $+2.9 \times 10^2 \text{ kJ}$

1b. -177 kJ

3a. $0.385 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ for Zn

3b. $0.13 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ for Pt

3c. $0.905 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ for Al

5. $545 \text{ }^\circ\text{C}$

7. $24.0 \text{ }^\circ\text{C}$

9. $2.3 \times 10^2 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$

11. 1.21 J/K

13. $2.49 \times 10^5 \text{ kJ}$ of heat evolved.

15a. 65.59 kJ

15b. $3.65 \times 10^3 \text{ kJ}$

15c. $1.45 \times 10^3 \text{ kJ}$

17a. 504 kg CH_4

17b. $-6.20 \times 10^5 \text{ kJ}$ of heat energy

17c. $2.90 \times 10^3 \text{ L H}_2\text{O}$

19. $1.36 \times 10^3 \text{ kJ}$ heat

21a. -5×10^1 kJ/mol

21b. The ΔT here is known to just one significant figure (0.9 °C). Doubling the amount of KOH should give a temperature change known to two significant figures (1.6 °C) and using twenty times the mass of KOH should give a temperature change known to three significant figures (16.0 °C).

23. 4.2×10^2 g NH_4Cl

25. -56 kJ/mol

27. 2.7×10^2 kJ heat evolved .

29. 39.6 g

31. 1.83 g H_2O

33. 0.111 L

35. 4.98 kJ /° C

37a. -2.34×10^3 kJ/mol $\text{C}_5\text{H}_{10}\text{O}_5$

37b. $\text{C}_5\text{H}_{10}\text{O}_5 (\text{g}) + 5\text{O}_2 (\text{g}) \rightarrow 5\text{CO}_2 (\text{g}) + 5\text{H}_2\text{O} (\text{l}) \quad \Delta H = -2.34 \times 10^3 \text{ kJ}$

39a. Endothermic

39b. +18 kJ/mol

41. 7.72 kJ/°C

43. 5.23°C

45. 15 g

47a. -3.4 L atm

47b. -3.5×10^2 J

47c. -83 cal

49. When the $\text{Ne}(\text{g})$ sample expands into an evacuated vessel it does not push aside any matter, hence no work is done.

51a. Work is done on the system by the surroundings (compression).

51b. No pressure-volume work is done.

51c. Work is done on the system by the surroundings (compression).

53. 3.21 L
- 55a. 0
- 55b. -562 J
- 55c. 0.08 kJ
- 57a. Yes
- 57b. Yes
- 57c. The temperature of the gas stays the same if the process is isothermal.
- 57d. ΔU for the gas must equal zero by definition (temperature is not changing).
59. This situation is impossible. An ideal gas expanding isothermally means that $\Delta U = 0 = q + w$, or $w = -q$, not $w = -2q$.
61. -545 J
63. According to the First Law of Thermodynamics, the answer is (c).
- 65a. -2008 kJ/mol
- 65b. -2012 kJ/mol
67. +30.74 kJ
69. $\Delta H^\circ = -290.$ kJ
71. $\Delta H^\circ = -217.5$ kJ
73. $\Delta H^\circ = -747.5$ kJ
75. $\Delta H^\circ = -35.8$ kJ
77. $\Delta H^\circ = -120.$ kJ
- 79a. -55.7 kJ
- 79b. -1124 kJ
81. -206.0 kJ/mol
83. +202.4 kJ
85. -1366.7 kJ
87. -102.9 kJ/mol
89. -55 kJ

91. $2.40 \times 10^6 \text{ kJ}$

93. $-424 \text{ kJ} = \Delta H_f^\circ [\text{HCOOH}(\text{s})]$

Integrative and Advanced Exercises

96. 3.5°C . This large a temperature rise is unlikely, as some of the kinetic energy will be converted into forms other than heat, such as sound and the fracturing of the object along with the surface it strikes. In addition, some heat energy would be transferred to the surface.

97. $-1.95 \times 10^3 \text{ kJ/mol } \text{C}_6\text{H}_8\text{O}_7$

103. The sewage gas.

107. $303 \text{ g } \text{C}_6\text{H}_{12}\text{O}_6$

109. The gas mixture contains 87.0% CH_4 and 13.0% C_2H_6 , both by volume.

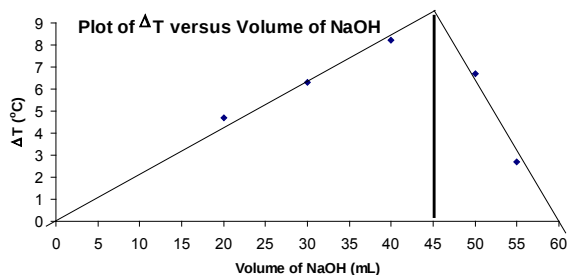
112. $\Delta H = -1.45 \times 10^3 \text{ kJ/mol}, 3 \text{ O}_2(\text{g}) + \text{C}_2\text{H}_6\text{O}(\text{g}) \rightarrow 2 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O}(\text{l}).$

113. 69 seconds

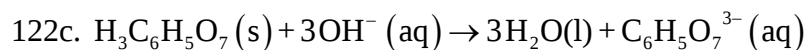
114. -12 J

Feature Problems

122a. The equivalence point occurs with 45.0 mL of 1.00 M NaOH(aq) [45.0 mmol NaOH] added and 15.0 mL of 1.00 M citric acid [15.0 mmol citric acid].

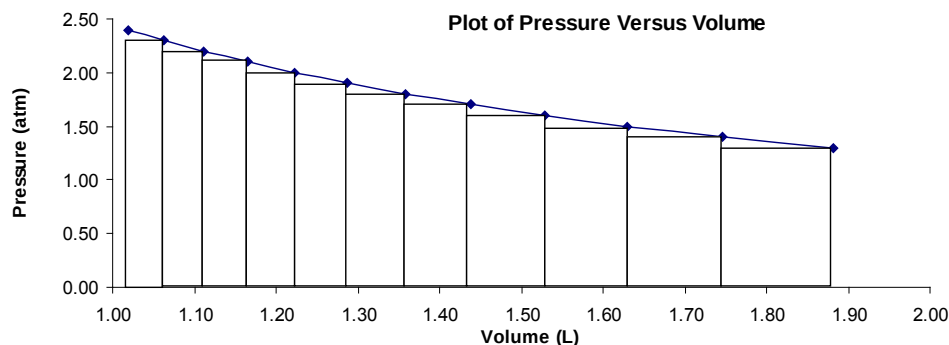


122b. Heat is a product of the reaction, as are chemical species (products). Products are maximized at the exact stoichiometric proportions. Since each reaction mixture has the same volume, and thus about the same mass to heat, the temperature also is a maximum at this point.



125a. -147 J

125b.



125c. $w = -152 \text{ J}$

125d. The maximum work is 209 J. The minimum work would be +152 J.

125e. $\Delta U = 0$. Because $\Delta U = q + w = 0$, $q = -w$. This means that -209 J corresponds to the maximum work of compression, and -152 J corresponds to the minimum work of compression.

125f. $q/T = nR \ln V_f/V_i$. Yes, q/T is a state function.

Self-Assessment Exercises

130. The answer is (b).

131. The answer is (c).

132. The answer is (d).

133. The answer is (a).

134. The answer is (b).

135. The answer is (a).

136. 52.7°C

137a. $2 \text{ N}_2 + \text{O}_2 \rightarrow 2 \text{ N}_2\text{O}$

137b. $\text{S} + \text{O}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$

137c. $2 \text{ CH}_3\text{CH}_2\text{COOH} + 7 \text{ O}_2 \rightarrow 6 \text{ CO}_2 + 6 \text{ H}_2\text{O}$

138. -218 kJ/mol

139. Enthalpy of formation for elements (even molecular ones, such as O_2 or Cl_2) is by convention set to 0. While it is possible for the enthalpy of formation of a compound to be near zero, it is unlikely.

140. From a theoretical standpoint, one can have a situation where the $\Delta U < 0$, but there is enough work done on the system that makes $\Delta H > 0$.

141. A gas stove works by combustion of a flammable fuel. Once shut off, the heat source instantly disappears. An electric stove works by the principle of heat conduction. Even after the electricity is shut off to the heating coil, it takes time for the coil to cool because of its heat capacity, and therefore it continues to supply heat to the pot.

142. The answer is (a).

143. The answer is (b).

Chapter 8 Answers

Practice Examples

1a. 4.34×10^{14} Hz

1b. 3.28 m

2a. 520 kJ/mol

2b. 4.612×10^{14} Hz (orange), 6.662×10^{14} Hz (indigo).

3a. Yes, This is E_9 for $n = 9$.

3b. $n = 7$

4a. 486.2 nm

4b. 121.6 nm (1216 angstroms)

5a. 80.13 nm

5b. Be^{3+}

6a. 1.21×10^{-43} m

6b. 3.96×10^4 m/s

7a. 6.4×10^{-43} m

7b. 1.3 m s^{-1}

8a. 0.167 out of 1, or 16.7%.

8b. 100 and 200 pm.

9a. 0.52 nm

9b. 150. pm

10a. Yes

10b. $\neq 1$ and 2

11a. 3p

11b. $n = 3$; $l = 0, 1, 2$; $m_l = -2, -1, 0, 1, 2$

12a. (3,2,-2,1) $m_s = 1$ is incorrect. The values of m_s can only be $+\frac{1}{2}$ or $-\frac{1}{2}$.
(3,1,-2, $\frac{1}{2}$) $m_l = -2$ is incorrect. The values of m_l can be +1,0,-1 when $l=1$
(3,0,0, $\frac{1}{2}$) All quantum numbers are allowed.

- (2,3,0, $\frac{1}{2}$) $\neq 3$ is incorrect. The value for l can not be larger than n .
 (1,0,0, $-\frac{1}{2}$) All quantum numbers are allowed.
 (2,-1,-1, $\frac{1}{2}$) $\neq -1$ is incorrect. The value for l can not be negative.

- 12b. (2,1,1,0) $m_s = 0$ is incorrect. The values of m_s can only be $+\frac{1}{2}$ or $-\frac{1}{2}$.
 (1,1,0, $\frac{1}{2}$) $\neq 1$ is incorrect. The value for l is 0 when $n=1$.
 (3,-1,1, $\frac{1}{2}$) $\neq -1$ is incorrect. The value for l can not be negative.
 (0,0,0, $-\frac{1}{2}$) $n = 0$ is incorrect. The value for n can not be zero.
 (2,1,2, $\frac{1}{2}$) $m_l = 2$ is incorrect. The values of m_l can be $+1, 0, -1$ when $l=1$.

13a. (a) and (c) are equivalent.

13b. excited state of a neutral species

14a. Ti

14b. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$. Each iodine atom has ten $3d$ electrons and one unpaired $5p$ electron.

15a. [Ar] $\begin{array}{|c|c|c|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$ $4s$

15b. [Xe] $\begin{array}{|c|c|c|c|c|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|c|c|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \uparrow \\ \hline \end{array}$ $4f$ $5d$ $6s$ $6p$

16a. (a) Tin is in the 5th period, hence, five electronic shells are filled or partially filled; (b) The $3p$ subshell was filled with Ar; there are six $3p$ electrons in an atom of Sn; (c) The electron configuration of Sn is [Kr] $4d^{10} 5s^2 5p^2$. There are no $5d$ electrons; (d) Both of the $5p$ electrons are unpaired, thus there are two unpaired electrons in a Sn atom.

16b. (a) The $3d$ subshell was filled at Zn, thus each Y atom has ten $3d$ electrons; (b) Ge is in the $4p$ row; each germanium atom has two $4p$ electrons; (c) We would expect each Au atom to have ten $5d$ electrons and one $6s$ electron. Thus each Au atom should have one unpaired electron.

Integrative Example

A. (a) 73.14 pm; (b) 17.7 K.

B. The possible combinations are $1s \rightarrow np \rightarrow nd$, for example, $1s \rightarrow 3p \rightarrow 5d$. The frequencies of these transitions are calculated as follows:

$$1s \rightarrow 3p: \nu = 2.92 \times 10^{15} \text{ Hz}$$

$$3p \rightarrow 5d: \nu = 2.34 \times 10^{14} \text{ Hz}$$

The emission spectrum will have lines representing $5d \rightarrow 4p$, $5d \rightarrow 3p$, $5d \rightarrow 2p$, $4p \rightarrow 3s$, $4p \rightarrow 2s$, $4p \rightarrow 1s$, $3p \rightarrow 2s$, $3p \rightarrow 1s$, and $2p \rightarrow 1s$. The difference between the sodium atoms is that the positions of the lines will be shifted to higher frequencies by 11^2 .

Exercises

1. 4.68 nm

3a. True

3b. False

3c. False

3d. True

5. Choice (c).

7. 8.3 min

9a. $6.9050 \times 10^{14} \text{ s}^{-1}$

9b. 397.11 nm

9c. $n = 10$

11a. $4.90 \times 10^{-18} \text{ J/photon}$

11b. 78.6 kJ/mol

13. $-1.816 \times 10^{-19} \text{ J}$, $2.740 \times 10^{14} \text{ s}^{-1}$

15. $n = 7.9 \approx 8$

17. 656.46 nm, 486.26 nm, 434.16 nm, 410.28 nm.

19a. $3.46 \times 10^{-19} \text{ J/photon}$

19b. $2.08 \times 10^5 \text{ J/mol}$

21. $2.1 \times 10^{-5} \text{ nm}$ radiation, has the greatest energy per photon. $4.1 \times 10^3 \text{ nm}$ has the least amount of energy per photon.

23. UV radiation

25a. $6.60 \times 10^{-19} \text{ J/photon}$

25b. Indium will display the photoelectric effect when exposed to ultraviolet light. It will not display the photoelectric effect when exposed to infrared light.

27a. 1.9 nm

27b. $-6.053 \times 10^{-20} \text{ J}$

29a. $1.384 \times 10^{14} \text{ s}^{-1}$

29b. 2166 nm

29c. Infrared radiation.

31a. $8.5 \times 10^{-10} \text{ m}$

31b. The electron in the hydrogen atom does not orbit at a radius of 4.00 Å.

31c. $-3.405 \times 10^{-20} \text{ J}$

31d. No

33. $n = 2$

35a. Line A is for the transition $n = 3 \rightarrow n = 1$, while Line B is for the transition $n = 4 \rightarrow n = 1$.

35b. Hydrogen atom

37a. Line A is for the transition $n = 5 \rightarrow n = 2$, while Line B is for the transition $n = 6 \rightarrow n = 2$.

37b. Be^{3+} cation

39. Electrons

41. $9.79 \times 10^{-35} \text{ m}$. The diameter of a nucleus approximates 10^{-15} m , which is far larger than the baseball's wavelength.

43. The Bohr model implies that the position of the electron is exactly known at any time in the future, once its position is known at the present. The distance of the electron from the nucleus, its energy, and the velocity of the electron in its orbit are also exactly known. All of these exactly known quantities can't, according to the Heisenberg uncertainty principle, be known with great precision simultaneously.

45. $\sim 1 \times 10^{-13} \text{ m}$

47. $1.4 \times 10^7 \text{ m s}^{-1}$

49. $\lambda \approx 17 \text{ cm}$

51. 0.55 nm

53. $n = 4.0$

55. Bohr orbits, as originally proposed, are circular, while orbitals can be spherical, or shaped like two tear drops or two squashed spheres, or shaped like four tear drops meeting at their

points. Bohr orbits are planar pathways, while orbitals are three-dimensional regions of space in which there is a high probability of finding electrons. The electron in a Bohr orbit has a definite trajectory. Its position and velocity are known at all times. The electron in an orbital, however, does not have a well-known position or velocity. Orbits and orbitals are similar in that the radius of a Bohr orbit is comparable to the average distance of the electron from the nucleus in the corresponding wave mechanical orbital.

57. Answer (c) is the only one that is correct.

59a. $5p$

59b. $4d$

59c. $2s$

61a. 1 electron

61b. 2 electrons

61c. 10 electrons

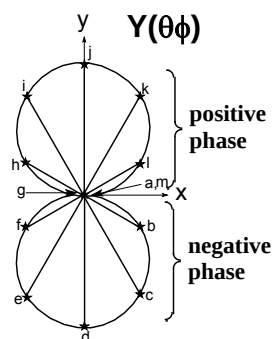
61d. 32 electrons

61e. 5 electrons

63. 106 pm

65. The angular part of the $2p_y$ wave function is $Y(\theta, \phi)_{py} = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi$. For all points in the xz plane $\phi = 0$, and since the sine of 0 is zero, this means that the entire xz plane is a node. Thus, the probability of finding a $2p_y$ electron in the xz plane is zero.

67.



69. A plot of radial probability distribution versus r/a_0 for a H_{1s} orbital shows a maximum at 1.0 (that is, $r = a_0$ or $r = 53$ pm).

71a. $3p$

71b. $3d$

71c. $6f$

73. $5d_{xyz}$

75a. three

75b. two

75c. zero

75d. fourteen

75e. two

75f. five

75g. 32

77. Configuration (b) is correct for phosphorus.

79a. 3

79b. ten

79c. two

79d. two

79e. fourteen

81a. Pb: $[\text{Xe}] 4f^{14}5d^{10}6s^26p^2$

81b. 114: $[\text{Rn}] 5f^{14}6d^{10}7s^27p^2$

83a. Excited state

83b. Excited state

83c. Ground state

83d. Excited state

85a. $[\text{Xe}]6s^24f^{14}5d^{10}$

85b. $[\text{Ar}]4s^2$

85c. $[\text{Xe}]6s^24f^{14}5d^{10}6p^4$

85d. $[\text{Kr}]5s^24d^{10}5p^2$

85e. $[\text{Xe}]6s^24f^{14}5d^3$

85f. $[\text{Kr}]5s^24d^{10}5p^5$

87a. rutherfordium

87b. carbon

87c. vanadium

87d. tellurium

87e. Not an element.

Integrative and Advanced Exercises

91a. Because the shortest wavelength of visible light is 390 nm, the photoelectric effect for mercury cannot be obtained with visible light.

91b. $2.02 \times 10^{-19} \text{ J}$

91c. $6.66 \times 10^5 \text{ m s}^{-1}$

92. $1.0 \times 10^{20} \frac{\text{photons}}{\text{sec}}$

93. Green

96. $m = 3$ and $n = 4$.

101. $4.8 \times 10^{-3} \text{ J}$

102. $7 \times 10^2 \text{ photons/s}$

105. 66.2 m/s

Feature Problems

114. Plot ν on the vertical axis and $1/n^2$ on the horizontal axis. The slope is $b = -3.2881 \times 10^{15} \text{ Hz}$ and the intercept is $8.2203 \times 10^{14} \text{ Hz}$.

116a. 121.5 nm and 102.6 nm.

116b. 97.2 nm, 486.1 nm, 1875 nm, 102.5 nm, 656.3 nm, 121.5 nm.

116c. The number of lines observed in the two spectra is not the same.

Self-Assessment Exercises

122. Atomic orbitals of multi-electron atoms resemble those of the H atom in having both angular and radial nodes. They differ in that subshell energy levels are not degenerate and their radial wave functions no longer conform to the expressions in Table 8.1.

123. Effective nuclear charge is the amount of positive charge from the nucleus that the valence shell of the electrons actually experiences. This amount is less than the actual nuclear charge, because electrons in other shells shield the full effect.

124. The p_x , p_y and p_z orbitals are triply degenerate (they are the same energy), and they have the same shape. Their difference lies in their orientation with respect to the arbitrarily assigned x, y, and z axes of the atom.

125. The difference between the 2p and 3p orbitals is that the 2p orbital has only one node ($n = 2 - 1$) which is angular, whereas the 3p orbital has two nodes, angular and radial

126. The answer is (a).

127a. Velocity of the electromagnetic radiation is fixed at the speed of light in a vacuum.

127b. Wavelength is inversely proportional to frequency.

127c. Energy is directly proportional to frequency.

128. Sir James Jeans's obtuse metaphor for the photoelectric effect points to the fact that it is a quantum-mechanical phenomenon. The photoelectric effect is a single photon-to-electron phenomenon; that is, a single photon that meets the minimum energy requirement can cause the ejection of an electron from the atom. If the photon is particularly energetic, the excess energy will not eject a second electron. Hence, you can't kill two birds with one stone. Furthermore, the atom cannot accumulate the energy from multiple photon hits to eject an electron: only one hit of sufficient energy equals one and only one ejection. Therefore, you can't kill a bird with multiple stones.

Chapter 9 Answers

Practice Examples

1a. S

1b. Ca

2a. V^{3+} (64 pm) < Ti^{2+} (86 pm) < Ca^{2+} (100 pm) < Sr^{2+} (113 pm) < Br^{-} (196 pm)

2b. As

3a. $K < Mg < S < Cl$

3b. Sb

4a. Cl and Al are paramagnetic; K^{+} , O^{2-} , and Zn are diamagnetic.

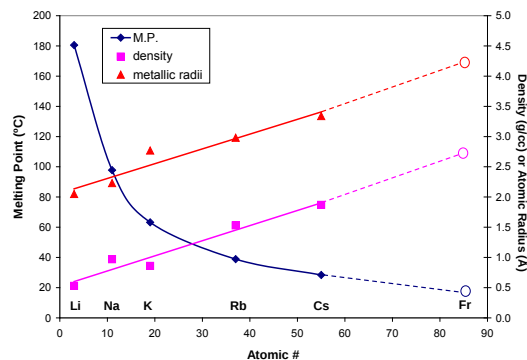
4b. Cr^{2+}

5a. 280 K

5b. 570 K

Integrative Example

A. Based on rough approximations of the trends of data, the properties of francium can be approximated. Melting point: 22 °C, density: 2.75 g/cc, atomic radius: 4.25 Å.



B. Element 168 should be a solid since the trend in boiling point and melting point would put the boiling point temperature above 298 K. The electronic configuration is $[Unk]10s^26h^8$.

Exercises

1. $14 \frac{g}{cm^3}$ to $16 \frac{g}{cm^3}$

3. A plot of density versus atomic number clearly shows that density is a periodic property for these two periods of main group elements. It rises, falls a bit, rises again, and falls back to the axis, in both cases.

5. Mendeleev arranged elements in the periodic table in order of increasing atomic weight. Atomic masses with non-integral values are permissible. Hence, there always is room for an added element between two elements that already are present in the table. On the other hand, Moseley arranged elements in order of increasing atomic number. Only integral (whole number) values of atomic number are permitted. Thus, when elements with all possible integral values in a certain range have been discovered, no new elements are possible in that range.

7a. 118

7b. 119

7c. $A_{119} \approx 298$ u and $A_{118} \approx 295$ u.

9a. Te

9b. K

9c. Cs

9d. N

9e. P

9f. Au

11. Sizes of atoms do not simply increase with atomic number is because electrons often are added successively to the same subshell. These electrons do not fully screen each other from the nuclear charge (they do not effectively get between each other and the nucleus). Consequently, as each electron is added to a subshell and the nuclear charge increases by one unit, all of the electrons in this subshell are drawn more closely into the nucleus, because of the ineffective shielding.

13a. B

13b. Te

15. $\text{Li}^+ < \text{Br} < \text{Se} < \text{I}^-$

17. Fe^{2+} and Co^{3+} , Sc^{3+} and Ca^{2+} , F^- and Al^{3+} , Zn^{2+} and Cu^+ .

19. Ions can be isoelectronic without having noble-gas electron configurations.

21. $\text{Cs} < \text{Sr} < \text{As} < \text{S} < \text{F}$

23. For an ionization potential, negatively charged electron is being separated from a positively charged cation, a process that must always require energy, because unlike charges attract each other.

25. 9951.5 kJ/mol

27. Exothermic

29. In the case of Na^+ , the electron is being removed from a species that is left with a 2+ charge, while in the case of Ne, the electron is being removed from a species with a 1+ charge. The more highly charged the resulting species, the more difficult it is to produce it by removing an electron.

31a. $\text{Al} < \text{Si} < \text{S} < \text{Cl}$

31b. $\text{Al} < \text{Si} < \text{S} < \text{Cl}$

33. Fe^{2+}

35a. Diamagnetic

35b. Paramagnetic

35c. Diamagnetic

35d. Diamagnetic

35e. Paramagnetic

35f. Diamagnetic

35g. Paramagnetic

37. All atoms with an odd number of electrons must be paramagnetic. There is no way to pair all of the electrons up if there is an odd number of electrons. Many atoms with an even number of electrons are diamagnetic, but some are paramagnetic.

39a. Elements that one would expect to exhibit the photoelectric effect with visible light should be ones that have a small value of their first ionization energy. Based on Figure 9-9, the alkali metals have the lowest first ionization potentials of these. Cs, Rb, and K are three suitable metals. Metals that would not exhibit the photoelectric effect with visible light are those that have high values of their first ionization energy. Again from Figure 9-9, Zn, Cd, and Hg seem to be three metals that would not exhibit the photoelectric effect with visible light.

39b. Rn

39c. +600 kJ/mol

39d. 5.7 g/cm^3

41a. 5.4 g/cm^3

41b. Ga_2O_3 , 74.5% Ga.

43. ~210 K

45a. Statement 1

45b. Statement 1

45c. Statement 3

45d. Statement 4

45e. Statement 2

45f. Statement 2

47. Ga^{4+} and Ge^{5+}

Integrative and Advanced Exercises

51. Both (b) and (e) are compatible with the sketch.

53. "Gruppe V" or "Gruppe VI."

55.

Element	Atomic Radius, pm	First Ionization Energy, kJ/mol
Ge	123	762
Al	same	same or smaller
In	larger	smaller
Se	smaller	larger

57. BrCl : melting point = 226 K, boiling point = 286 K
 ICl : melting point = 280 K, boiling point = 348 K

61a. A

61b. B

61c. A

61d. B

62. Since $(0.3734)(382) = 143$ u, if we subtract 143 from 382 we get 239 u, which is very close to the correct value of 238 u. First we convert to $\text{J/g}^\circ\text{C}$: $0.0276 \times (4.184 \text{ J/cal}) = 0.1155 \text{ J/g}^\circ\text{C}$, so: $0.1155 = 0.011440 + (23.967/\text{atomic mass})$; solving for atomic mass yields a value of 230 u, which is within about 3% of the correct value.

$$65. E_1 = E_1 \times N_A = \frac{8.716 \times 10^{-18}}{1 \text{ atom}} \times \frac{6.022 \times 10^{23}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 5249 \text{ kJ/mol}$$

$$66. I_1 \text{ for F (1681)} \approx I_2 \text{ for Ba (965)} < I_3 \text{ for Sc (2389)} < I_2 \text{ for Na (4562)} < I_3 \text{ for Mg (7733)}$$

Feature Problems

70. $A = 2.30 \times 10^{15} \text{ Hz}$ and $b = 0.969$. The value of A (calculated in this question) is close to the Rydberg frequency ($3.2881 \times 10^{15} \text{ s}^{-1}$), so it is probably the equivalent term in the Moseley equation. The constant b , which is close to unity, could represent the number of electrons left in the K shell after one K-shell electron has been ejected by a cathode ray. Thus, one can think of b as representing the screening afforded by the remaining electron in the K-shell.

71a. $[\text{Ne}]3p^1 = 293 \text{ kJ mol}^{-1}$, $[\text{Ne}]4s^1 = 188 \text{ kJ mol}^{-1}$, $[\text{Ne}]3d^1 = 147 \text{ kJ mol}^{-1}$, $[\text{Ne}]4p^1 = 134 \text{ kJ mol}^{-1}$.

71b. $[\text{Ne}]3p^1 : Z_{\text{eff}} = 1.42$, $[\text{Ne}]4s^1 : Z_{\text{eff}} = 1.51$, $[\text{Ne}]3d^1 : Z_{\text{eff}} = 1.00$, $[\text{Ne}]4p^1 : Z_{\text{eff}} = 1.28$.

71c. $[\text{Ne}]3p^1 : \bar{r}_{3p} = 466 \text{ pm}$, $[\text{Ne}]4s^1 : \bar{r}_{4s} = 823 \text{ pm}$, $[\text{Ne}]3d^1 : \bar{r}_{3d} = 555 \text{ pm}$, $[\text{Ne}]4p^1 : \bar{r}_{4p} = 950 \text{ pm}$.

71d. The more deeply an orbital penetrates (i.e., the closer the orbital is to the nucleus), the greater is the effective nuclear charge felt by the electrons in that orbital. It follows then that the $4s$ orbital will experience the greatest effective nuclear charge and that the Z_{eff} values for the $3p$ and $4p$ orbitals should be larger than the Z_{eff} for the $3d$ orbital.

Self-Assessment Exercises

77. The answer is (b).

78. The answer is (a).

79. The answer is (a).

80. The answer is (b).

81. The answer is (a).

82. The answer is (d).

83. $\text{Cs}^+ : [\text{Xe}]$, or $[\text{Kr}] 5s^2 4d^{10} 5p^6$, $\text{Cs}^{2+} : [\text{Kr}] 5s^2 4d^{10} 5p^5$

84. The first ionization energy of Mg is higher than Na because, in the case of Mg, an electron from a filled subshell is being removed, whereas in Na, the removing of one electron leads to the highly stable electron configuration of Ne. The second ionization of Mg is lower than Na, because in the case Mg, the electron configuration of Ar is achieved, whereas in Na, the stable [Ar] configuration is being lost by removing an electron from the filled subshell.

85a. As

85b. F^-

85c. Cl^-

85d. Carbon

85e. Carbon

86. The trends would generally follow higher first ionization energy values for a fuller subshell. The exception is the case of S and P, where P has a slightly higher value. This is because there is a slight energy advantage to having a half-filled subshell with an electron in each of p_x , p_y and p_z orbitals as in the case of P, whereas the S has one extra electron.

87. The pairs are Ar/Ca, Co/Ni, Te/I and Th/Pa.

88a. protons = 50

88b. neutrons = 69

88c. $4d$ electrons = 10

88d. $3s$ electrons = 2

88e. $5p$ electrons = 2

88f. valence shell electrons = 4

89a. F

89b. Sc

89c. Si

90a. C

90b. Rb

90c. At

91a. Ba

91b. S

91c. Bi

92. $\text{Rb} > \text{Ca} > \text{Sc} > \text{Fe} > \text{Te} > \text{Br} > \text{O} > \text{F}$

93a. False

93b. True

93c. True

93d. True

93e. True

94a. False

94b. False

94c. True

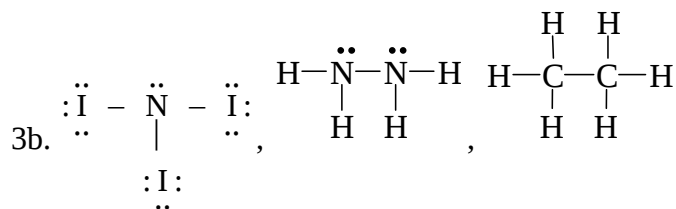
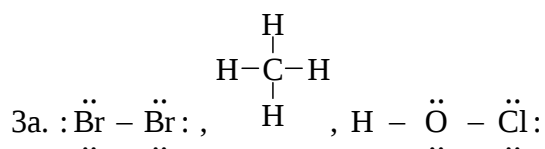
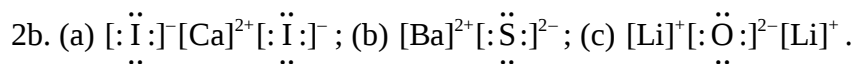
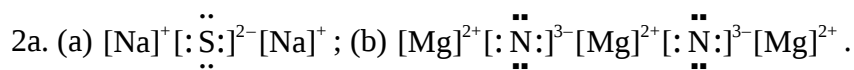
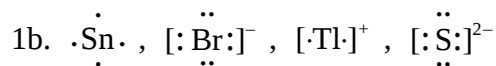
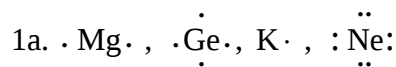
94d. True

95. These ionization energies are the reverse of electron affinities.

96. Ionization energy generally increases with Z for a given period.

Chapter 10 Answers

Practice Examples

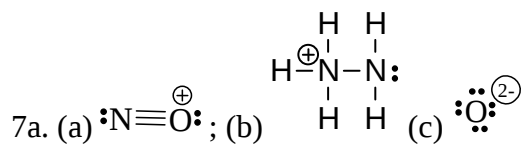
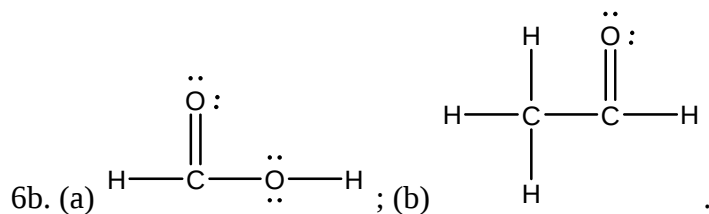
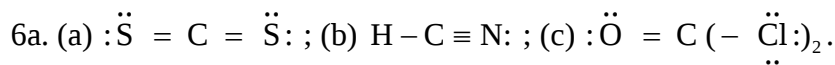


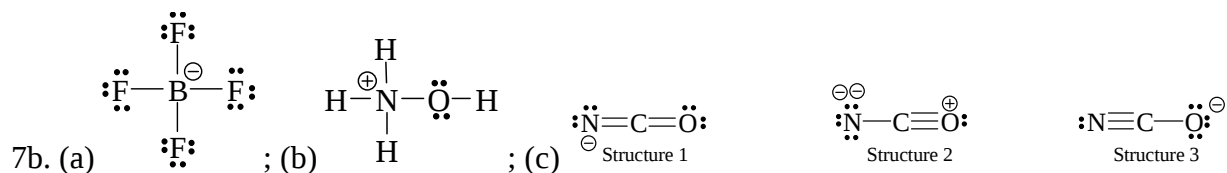
4a. N—H and P—Cl bonds are the most polar of the four bonds cited.

4b. The P—O bond is the most polar of the four bonds cited.

5a. The electrostatic potential map that corresponds to IF is the one with the most red in it.

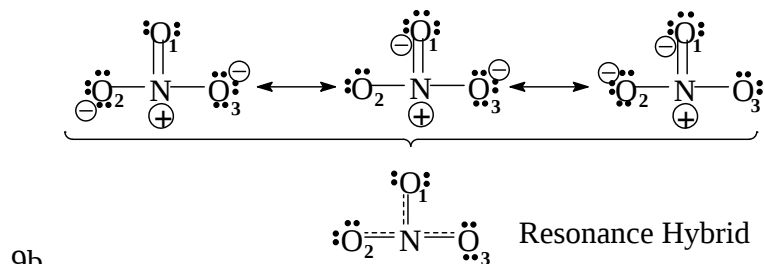
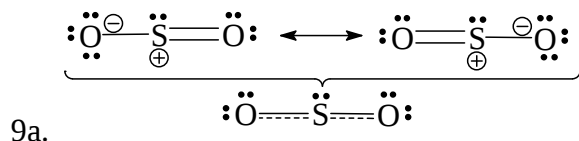
5b. The electrostatic potential map that corresponds to CH₃OH is the one with the most red in it.





8a. $\begin{array}{c} \text{:}\ddot{\text{N}}=\ddot{\text{O}}-\ddot{\text{Cl}}\text{:} \\ \ominus \quad \oplus \end{array}$ is much poorer than the one derived in Example 10-8 because it has a positive formal charge on oxygen, which is the most electronegative atom in the molecule.

8b. $\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{C}\equiv\text{N}\text{:} \\ | \\ \text{H} \end{array}$ and $\begin{array}{c} \text{H}-\text{N}^{\oplus}=\text{C}=\ddot{\text{N}}^{\ominus} \\ | \\ \text{H} \end{array}$. The first structure is the better of the two structures because it has no formal charges.

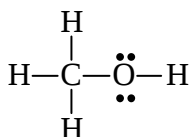


10a. Trigonal pyramidal

10b. Tetrahedral

11a. Linear

11b. Linear



12a. . The H—C—H bond angles are $\sim 109.5^\circ$, as are the H—C—O bond angles. Around the O there are two bonding pairs of electrons and two lone pairs, resulting in a tetrahedral electron-group geometry and a bent molecular shape around the O atom, with a C—O—H bond angle of slightly less than 109.5° .

12b. . The H—N—H bond angle and the H—N—C bond angles are almost the tetrahedral angle of 109.5° , made a bit smaller by the lone pair. The H—C—N angles, the H—C—H angle and the H—C—C angles all are very close to 109.5° . The C—O—H bond angle is made somewhat smaller than 109.5° by the presence of two lone pairs on O. Three electron groups surround the right-hand C, making its electron-group and molecular geometries trigonal planar. The O—C—O bond angle and the O—C—C bond angles all are very close to 120° .

13a. In H_2O_2 , the molecular geometry around each O atom is bent; the bond moments do not cancel. H_2O_2 is polar.

13b. PCl_5 as the only nonpolar species; it is a highly symmetrical molecule in which individual bond dipoles cancel out.

14a. From Table 10.2, the length of a C—H bond is 110 pm. The length of a C—Br bond is not given in the table. A reasonable value is the average of the C—C and Br—Br bond lengths = 195 pm.

14b. $|\bar{\text{S}} - \text{C} \equiv \text{N}|$, linear.

15a. -486 kJ/mol

15b. $-4 \times 10^1 \text{ kJ/mol NH}_3$

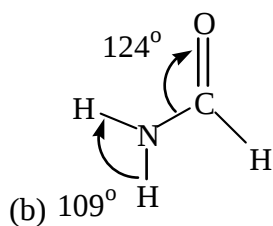
16a. Exothermic

16b. Endothermic

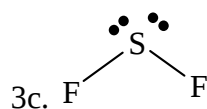
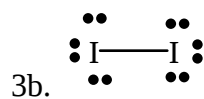
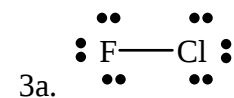
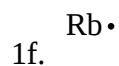
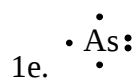
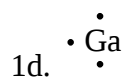
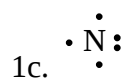
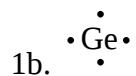
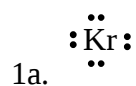
Integrative Example

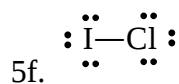
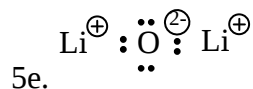
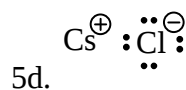
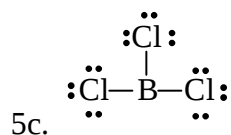
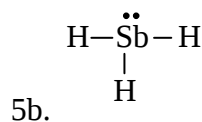
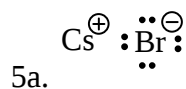
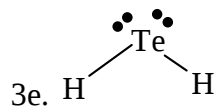
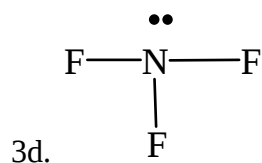
A $\text{P}-\text{Cl} = -165.5 \text{ kJ/mol}$. Since the geometries of the two molecules differ, the orbital overlap between P and the surrounding Cl atoms will be different and therefore the P—Cl bonds in these two compounds will also be slightly different.

B. (a) Formamide: $\text{H}_2\ddot{\text{N}}-\text{C}(=\text{O})-\text{H}$, bond energy = 2233 kJ/mol ; Formaldoxime: $\text{H}_2\text{C}=\ddot{\text{N}}-\text{OH}$, bond energy = 2129 kJ / mol . Since BE of formamide is greater than that of formaldoxime, it is more stable, and its conversion endothermic.



Exercises



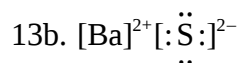


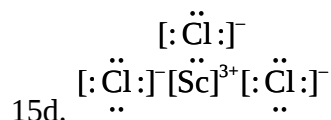
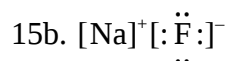
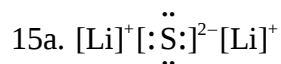
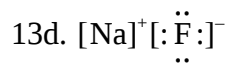
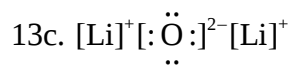
7. NO_2 , BF_3 , SF_6 .

9a. Has two bonds (4 electrons) to the second hydrogen, and only six electrons around the nitrogen.

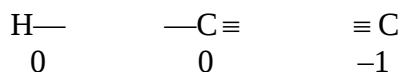
9b. It is improperly written as a covalent Lewis structure. CaO is actually an ionic compound.

11. The answer is (c). The flaws with the other answers are as follows: (a) C does not have an octet of electrons; (b) Neither C has an octet of electrons and the total number of valence electrons is incorrect; (c) The total number of valence electrons is incorrect.

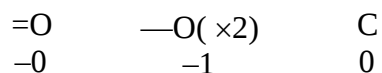




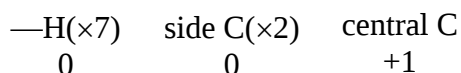
17a.



17b.



17c.



19. For instance, there are cases where atoms of the same type with the same oxidation state have different formal charges, such as oxygen in ozone, O_3 . Another is that formal charges are used to decide between alternative Lewis structures, while oxidation state is used in balancing equations and naming compounds. Also, the oxidation state in a compound is invariant, while the formal charge can change. The most significant difference, though, is that whereas the oxidation state of an element in its compounds is usually not zero, its formal charge usually is.

21a. +1

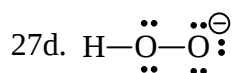
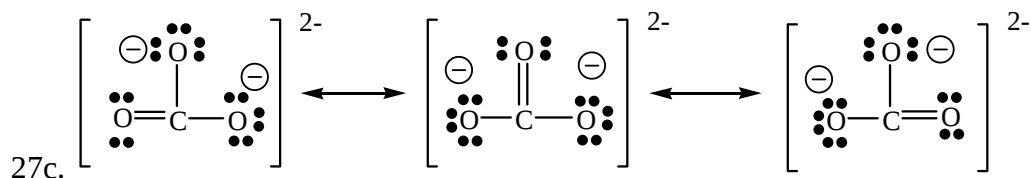
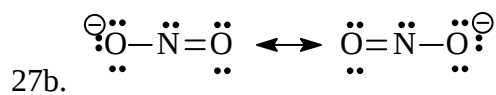
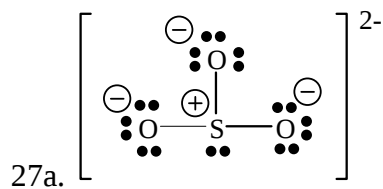
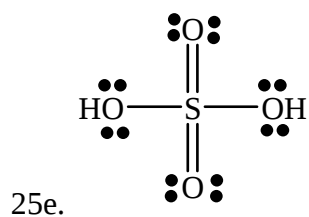
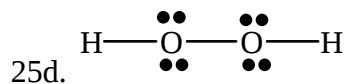
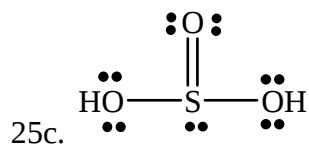
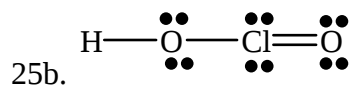
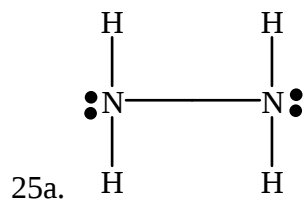
21b. -1

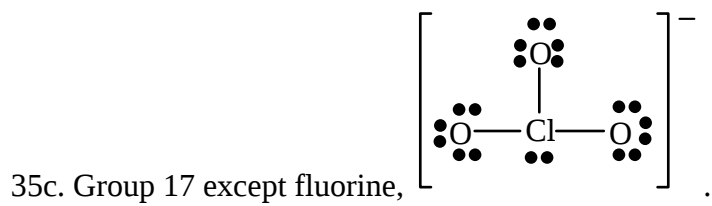
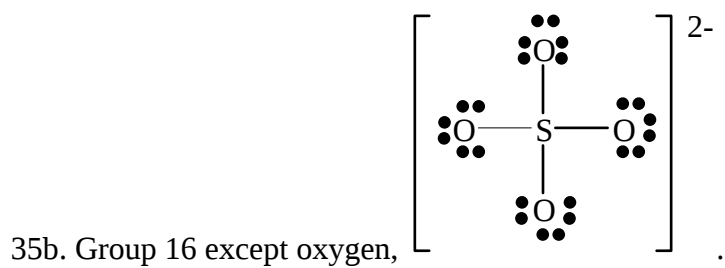
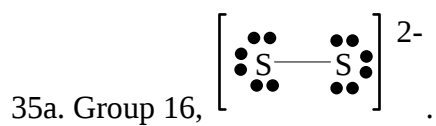
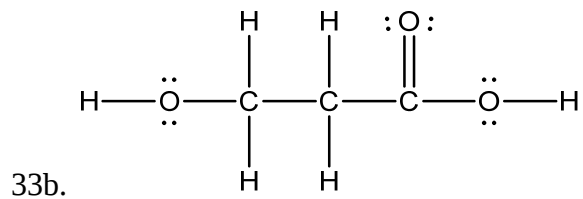
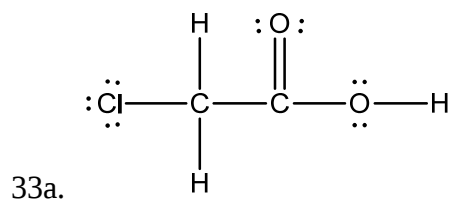
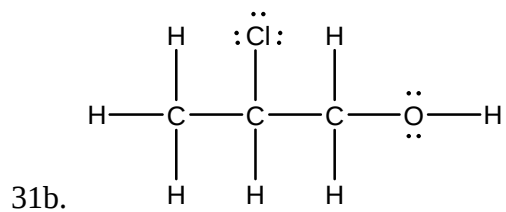
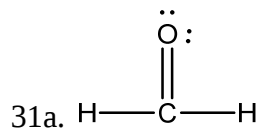
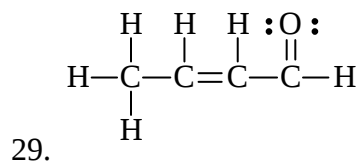
21c. 0

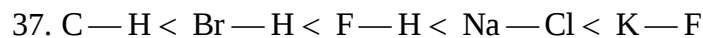
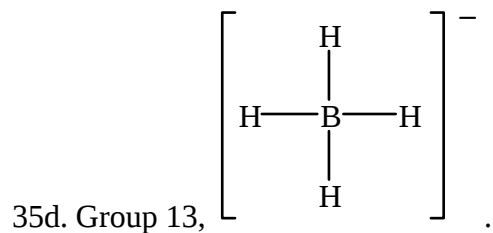
21d. -2

21e. 0

23. Based on formal charge rules alone, we must conclude that structures (A) and (B) are equally plausible.







39a. 4%

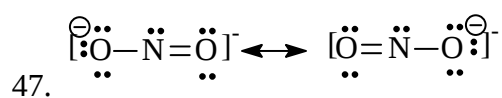
39b. 5%

39c. 60%

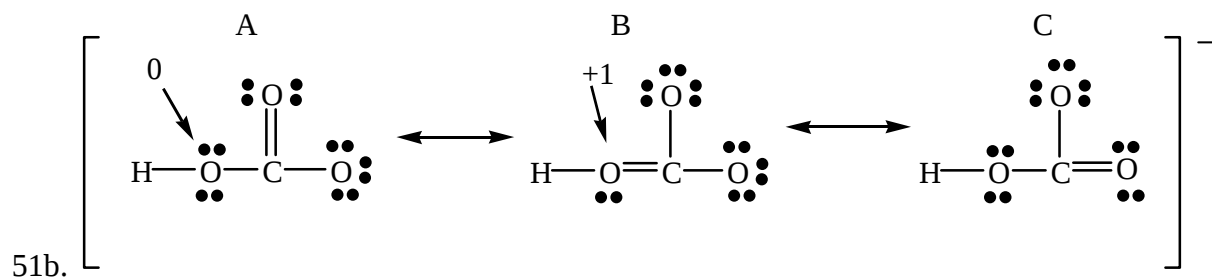
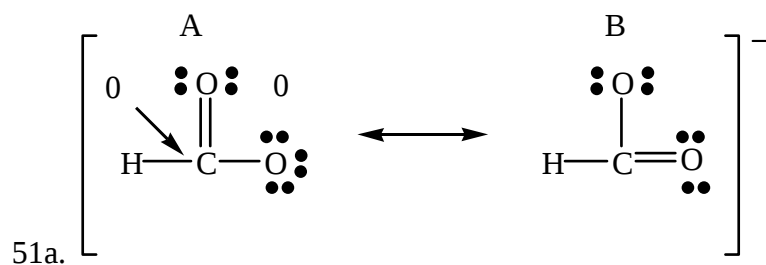
39d. 33%

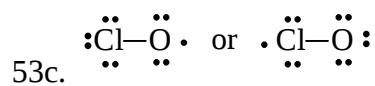
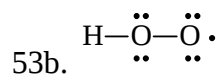
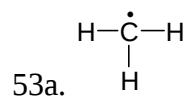
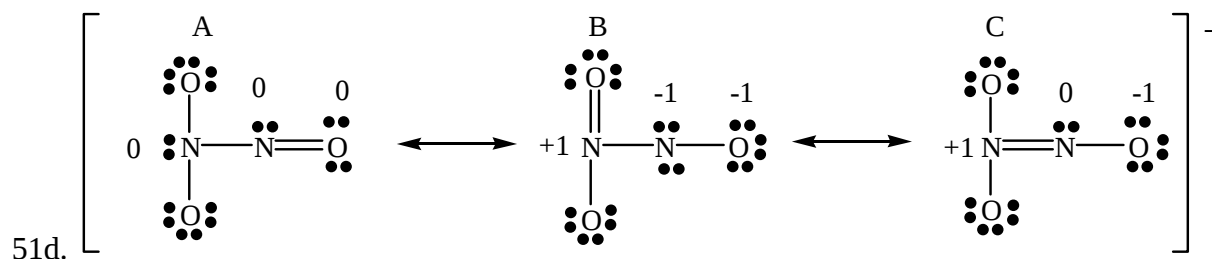
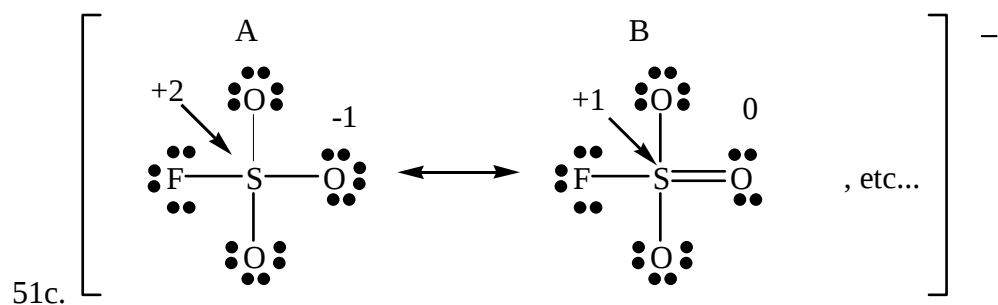
43. $\text{F}_2\text{C}=\text{O}$ is represented on the left, while $\text{H}_2\text{C}=\text{O}$ is represented on the right.

45. The molecular formulas for the compounds are SF_4 and SiF_4 . The electrostatic potential map on the right is for SiF_4 .



49. The molecule seems best represented as a resonance hybrid of (a) and (b).





55a. Diamagnetic

55b. Paramagnetic

55c. Paramagnetic

55d. Diamagnetic

55e. Diamagnetic

55f. Paramagnetic

57. SF_4 and ICl_3 require expanded octets. The others do not.

59a. Linear

59b. Linear

59c. Tetrahedral

59d. Trigonal Planar

59e. Bent

61a. Bent

61b. Planar

61c. Linear

61d. Octahedral

61e. Tetrahedral

63. CO_3^{2-}

65a. $\text{O}=\text{C}=\text{O}$, linear.

65b. $\begin{array}{c} \text{O} \\ || \\ \text{Cl}-\text{C}-\text{Cl} \end{array}$, trigonal planar.

65c. $\begin{array}{c} \text{O} \\ || \\ \text{Cl}-\text{N}-\text{O} \end{array}$

67a. Tetrahedral

67b. Tetrahedral

67c. Octahedral

67d. Linear

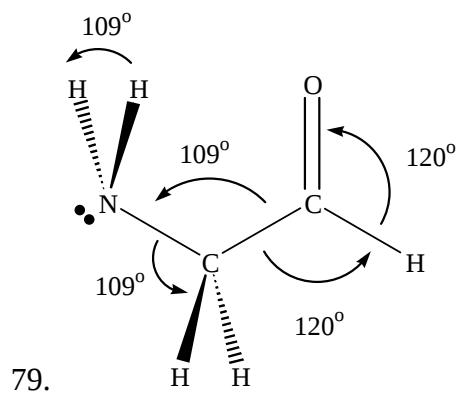
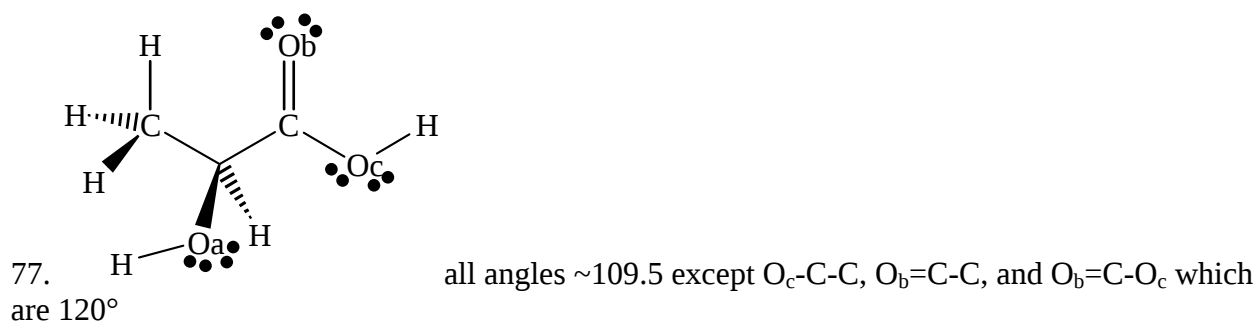
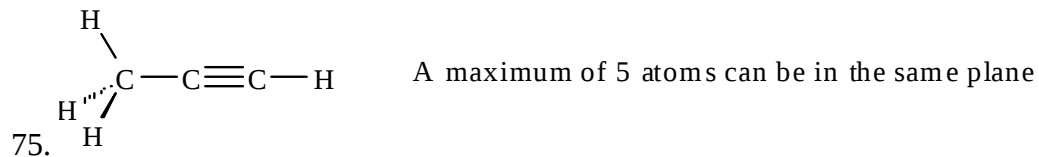
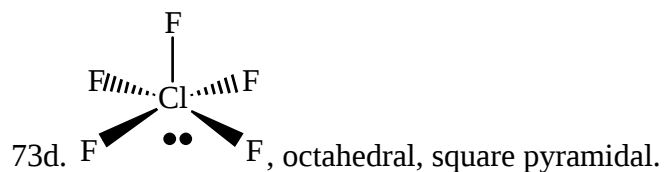
69. Tetrahedral

71. Looking at the structures, the molecular angle/shape depends on the number of valence electron pairs on the central atom. The more pairs there are, the more acute the angle becomes.

73a. $\begin{array}{c} \cdot \\ \cdot \\ \text{F}-\text{Cl}-\text{F} \\ \cdot \\ \cdot \end{array}$, trigonal bipyramidal, linear.

73b. $\begin{array}{c} \cdot \\ \cdot \\ \text{F}-\text{Cl}-\text{F} \\ | \\ \text{F} \end{array}$, trigonal bipyramidal, t-shaped.

73c. $\begin{array}{c} \cdot \\ \cdot \\ \text{F} \diagup \text{Cl} \diagdown \text{F} \\ \cdot \end{array}$, octahedral, square planar.



81a. Bent, polar.

81b. Trigonal pyramidal, polar.

81c. Bent, polar.

81d. Planar, nonpolar.

81e. Octahedral, nonpolar.

81f. Tetrahedral, polar.

83. It cannot be linear.

85. Br_2 possess the longest bond. Single bonds are generally longer than multiple bonds.

87a. 233 pm

87b. 172 pm

87c. 149 pm

87d. 191 pm

89. 144 pm

91. Endothermic

93. -113 kJ/mol

95a. $\Delta H_f^\circ = 39 \text{ kJ/mol}$

95b. $\Delta H_f^\circ = 99 \text{ kJ}$

97. -166 kJ/mol

99. 448 kJ/mol

Integrative and Advanced Exercises

101. -744 kJ/mol

104. 42.0 g/mol , C_3H_6 .

106. $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}, \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{H} \\ | \\ \text{H} \end{array}$. Neither is completely linear.

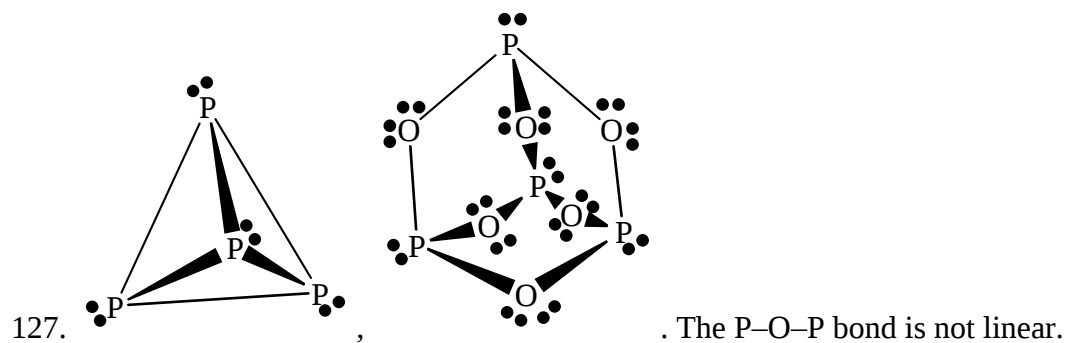
109. $\text{H}-\text{N}=\text{N}=\text{N}$, $\text{H}-\text{N}\equiv\text{N}$.

110. Bent

113. $+103 \text{ kJ}$

116. 307 kJ

120. $F = 0.00199$, $\text{Cl} = 0.00187$, $\text{Br} = 0.00191$, $\text{I} = 0.00192$. $EA \sim -260 \text{ kJ/mol}$. EA for At : $\sim -260 \text{ kJ/mol}$.



128a. 91 kJ/mol

128b. $\Delta EN = 0.97$

128c. 23%

129a. 1.49 D

129b. Approximately 92° .

129c. 97.6°

Self-Assessment Exercises

134. The answer is (b).

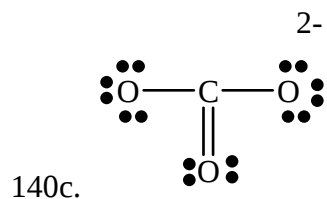
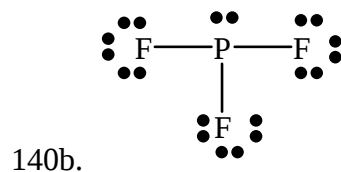
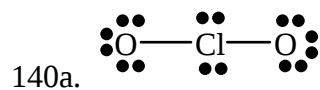
135. The answer is (c).

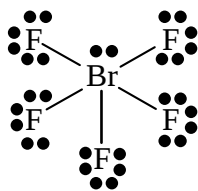
136. The answer is (a).

137. The answer is (a).

138. The answer is (b).

139. The answer is (c).





140d.

141a. Bent

141b. Trigonal pyramidal

141c. Tetrahedral

142. Bi

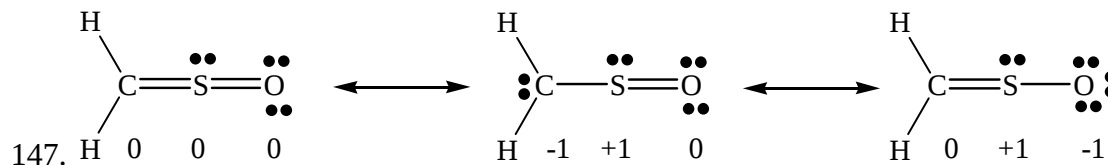
143.

Bond	Bond Energy (kJ/mol)	Bond Length (pm)
C–H	414	110
C=O	736	120
C–C	347	154
C–Cl	339	178

144. VSEPR theory is valence shell electron pair repulsion theory. It is based on the premise that electron pairs assume orientations about an atom to minimize electron pair repulsions.

145. Since there are 4 electron pairs around the central atom, the way to maximize the distance between them is to set up a tetrahedral electron group geometry. However, since there are only three atoms bonding to the central atom, the molecular geometry is trigonal pyramidal.

146. A pyramidal geometry is observed when an atom has one lone pair and is bonded to three other atoms (AX_3E). A bent geometry is observed when an atom has two lone pairs and is bonded to two other atoms (AX_2E_2). For both, the bond angles will be approximately (usually smaller than) 109° .



Chapter 11 Answers

Practice Examples

1a. There are three half-filled $2p$ orbitals on N, and one half-filled $5p$ orbital on I. Each half-filled $2p$ orbital from N will overlap with one half-filled $5p$ orbital of an I. Thus, there will be three N—I bonds. The I atoms will be oriented in the same direction as the three $2p$ orbitals of N: toward the x -, y -, and z -directions of a Cartesian coordinate system. Thus, the I—N—I angles will be approximately 90° (probably larger because the I atoms will repel each other). The three I atoms will lie in the same plane at the points of a triangle, with the N atom centered above them. The molecule is trigonal pyramidal.

1b. There are three half-filled orbitals on N and one half-filled orbital on each H. There will be three N—H bonds, with bond angles of approximately 90° . The molecule is trigonal pyramidal. (We obtain the same molecular shape if N is assumed to be sp^3 hybridized, but bond angles are closer to 109.5° , the tetrahedral bond angle.) VSEPR theory begins with the Lewis structure and notes that there are three bond pairs and one lone pair attached to N. This produces a tetrahedral electron pair geometry and a trigonal pyramidal molecular shape with bond angles a bit less than the tetrahedral angle of 109.5° because of the lone pair. Since VSEPR theory makes a prediction closer to the experimental bond angle of 107° , it seems more appropriate in this case.

2a. Bent molecular geometry, sp^3 hybridization.

2b. See-saw molecular geometry, sp^3d hybridization.

3a. Each central atom is surrounded by four electron pairs, requiring sp^3 hybridization. The carbon atoms have tetrahedral geometry, the oxygen atom is bent.

3b. The left-most C and the right-most O are surrounded by four electron pairs, and thus require sp^3 hybridization. The central carbon is surrounded by three electron groups and is sp^2 hybridized.

4a. There are four bond pairs around the left-hand C, requiring sp^3 hybridization. Three of the bonds that form are C—H sigma bonds resulting from the overlap of a half-filled sp^3 hybrid orbital on C with a half-filled $1s$ orbital on H. The other C has two attached electron groups, utilizing sp hybridization. The two C atoms join with a sigma bond: overlap of sp^2 on the left-hand C with sp on the right-hand C. The three bonds between C and N consist of a sigma bond (sp on C with sp on N), and two pi bonds ($2p$ on C with $2p$ on N).

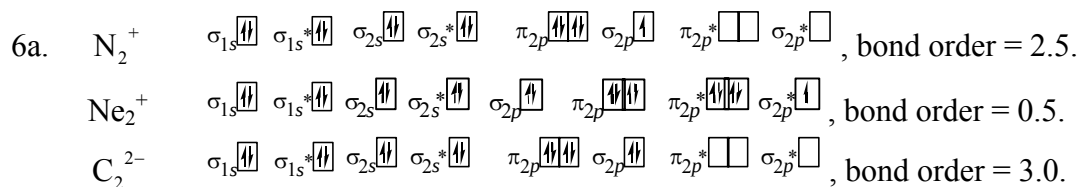
4b. structure(1) $| N_a \equiv N_b^{\oplus} - \bar{O} | \leftrightarrow | \underline{N}_a = N_b^{\oplus} = \bar{O} |$ structure(2). In both structures,

the central N is attached to two other atoms, and possesses no lone pairs. The geometry of the molecule thus is linear and the hybridization on this central N is sp . In structure (1) the $N \equiv N$ bond results from the overlap of three pairs of half-filled orbitals: (1) sp_x on N_b with $2p_x$ on N_a forming a σ bond, (2) $2p_y$ on N_b with $2p_y$ on N_a forming a π bond, and (3) $2p_z$ on N_b

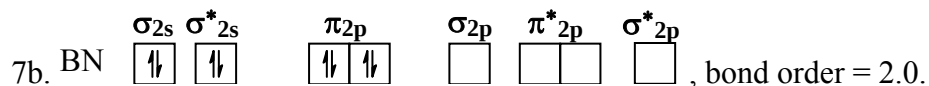
with $2p_z$ on N_a also forming a π bond. The N—O bond is a coordinate covalent bond, and forms by the overlap of the full sp_x orbital on N_b with the empty $2p$ orbital on O. In structure (2) the $N=O$ bond results from the overlap of two pairs of half-filled orbitals: (1) sp_y on N_b with $2p_y$ on O forming a σ bond and (2) $2p_z$ on N_b with $2p_z$ on O forming a π bond. The $N=N$ σ bond is a coordinate covalent bond, and is formed by two overlaps: (1) the overlap of the full sp_y orbital on N_b with the empty $2p_y$ orbital on N_a to form a σ bond, and (2) the overlap of the half-filled $2p_x$ orbital on N_b with the half-filled $2p_x$ orbital on N_a to form a π bond. Based on formal charge arguments, structure (1) is preferred, because the negative formal charge is on the more electronegative atom, O.

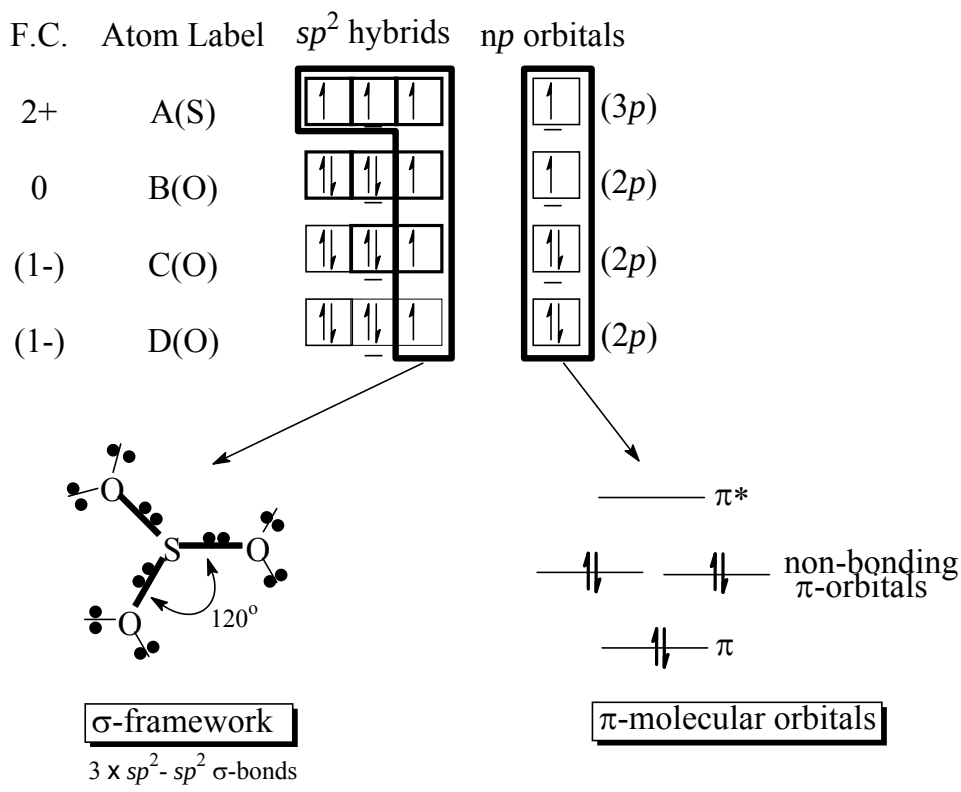
5a. 53 kJ/mol Li_2^+

5b. The bond order in H_2^- is $1/2$. We would expect the ion H_2^- to be stable, with a bond strength about half that of a hydrogen molecule.

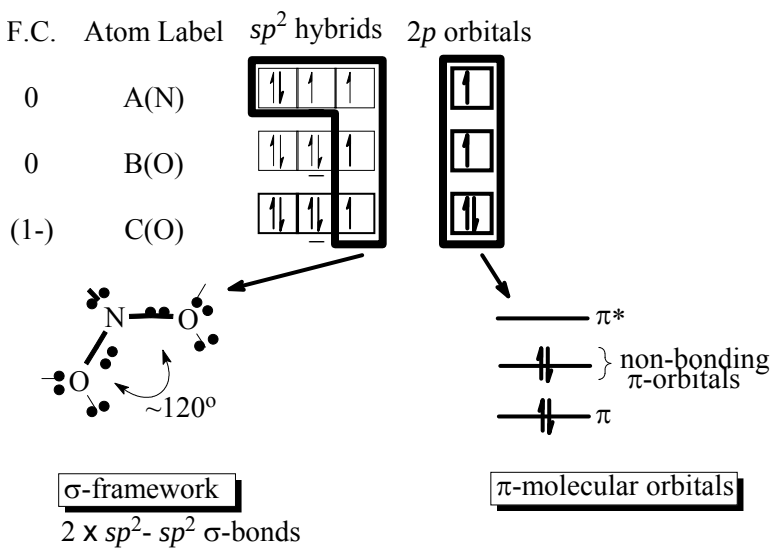


6b. The bond length increases as the bond order decreases. Longer bonds are weaker bonds.



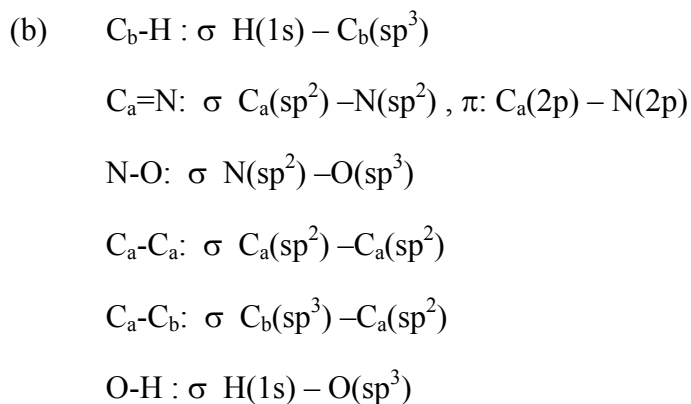
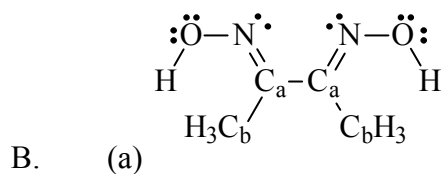
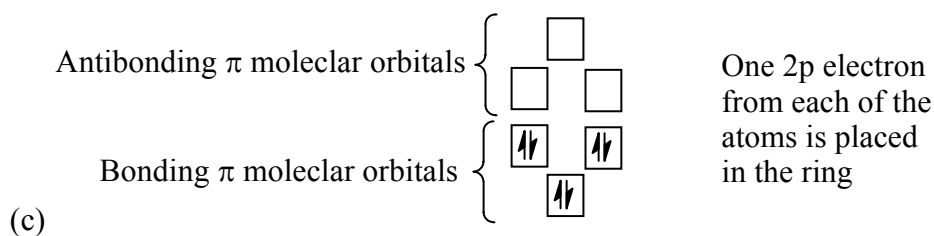
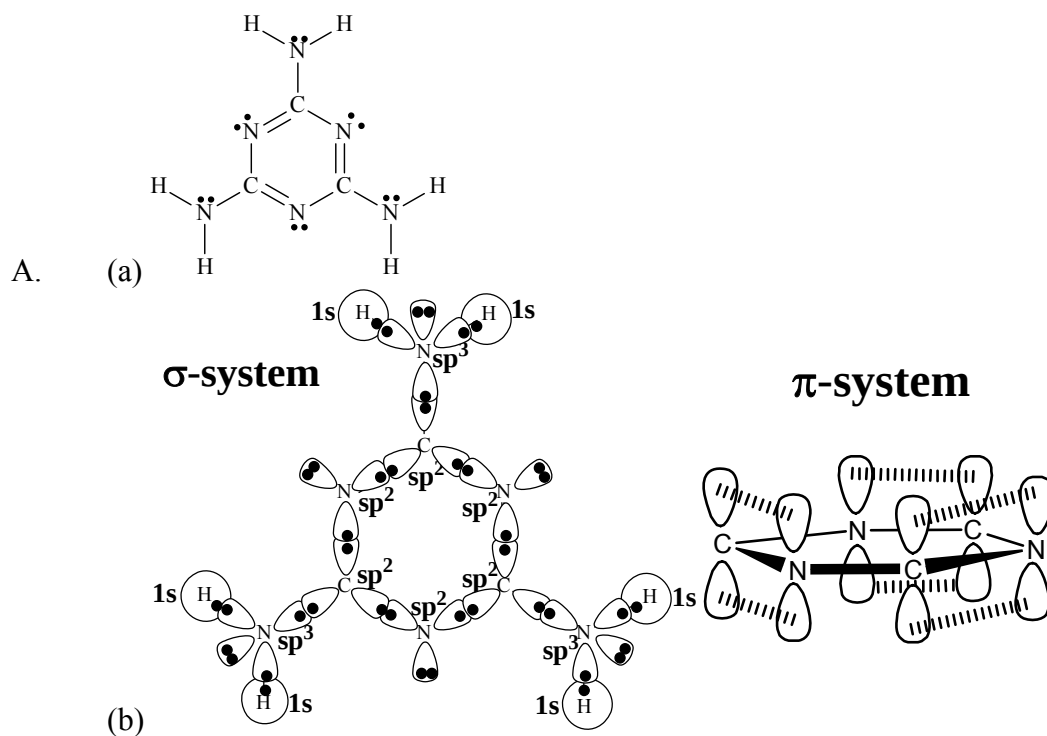


8a.



8b.

Integrative Example



Exercises

1. First, valence-bond theory clearly distinguishes between sigma and pi bonds. In valence-bond theory, it is clear that a sigma bond must be stronger than a pi bond, for the orbitals overlap more effectively in a sigma bond (end-to-end) than they do in a pi bond (side-to-side). *Second*, molecular geometries are more directly obtained in valence-bond theory than in Lewis theory. *Third*, Lewis theory does not explain hindered rotation about double bonds.

3a. Lewis theory does not describe the shape of the water molecule.

3b. In valence-bond theory using simple atomic orbitals, each H—O bond results from the overlap of a 1s orbital on H with a 2p orbital on O. The angle between 2p orbitals is 90° so this method initially predicts a 90° bond angle.

3c. In VSEPR theory the H₂O molecule is categorized as being of the AX₂E₂ type. The lone pairs repel each other more than do the bond pairs, explaining the smaller than 109.5° tetrahedral bond angle.

3d. In valence-bond theory using hybrid orbitals, each H—O bond results from the overlap of a 1s orbital on H with an sp³ orbital on O. The angle between sp³ orbitals is 109.5°.

5. The central atom is sp² hybridized in SO₂, CO₃²⁻, and NO₂⁻.

7a. C is the central atom. The molecule is linear and C is sp hybridized.

7b. N is the central atom. The molecule is trigonal planar around N which is sp² hybridized.

7c. Cl is the central atom. The electron-group geometry around Cl is tetrahedral, indicating that Cl is sp³ hybridized.

7d. B is the central atom. The electron-group geometry is tetrahedral, indicating that B is sp³ hybridized.

9. The hybridization is sp³d. Each of the three sigma bonds are formed by the overlap of a 2p orbital on F with one of the half-filled dsp³ orbitals on Cl. The two lone pairs occupy dsp³ orbitals.

11a. sp³d².

11b. sp

11c. sp³.

11d. sp².

11e. sp³d.

13a. Planar molecule. The hybridization on C is sp^2 .

13b. Linear molecule. The hybridization for each C is sp .

13c. Neither linear nor planar. The shape around the left-hand C is tetrahedral and that C has sp^3 hybridization.

13d. Linear molecule. The hybridization for C is sp .

15a. $\text{H}-\text{C}\equiv\text{N}|$. The $\text{H}-\text{C}$ bond is a σ bond, and the $\text{C}\equiv\text{N}$ bond is composed of 1 σ and 2 π bonds.

15b. $:\text{N}\equiv\text{C}-\text{C}\equiv\text{N}|$ The $\text{C}-\text{C}$ bond is a σ bond, and each $\text{C}\equiv\text{N}$ bond is composed of 1 σ and 2 π bonds.

15c.
$$\begin{array}{ccccccc} & \text{H} & & & \text{Cl} & & \\ & | & & & | & & \\ \text{H} & -\text{C} & - & \text{C} & = & \text{C} & - & \text{C} & - & \text{Cl} \\ & | & & | & & | & & | & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{Cl} & & \end{array}$$
 . All bonds are σ bonds except one of the bonds that comprise the $\text{C}=\text{C}$ bond. The $\text{C}=\text{C}$ bond is composed of one σ and one π bond.

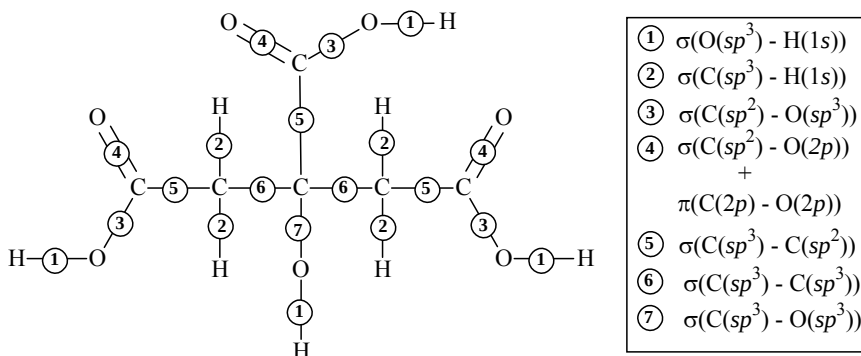
15d. $\text{H}-\text{O}=\text{N}=\text{O}$. All single bonds in this structure are σ bonds. The double bond is composed of one σ and one π bond.

17a. The geometry at C is tetrahedral; C is sp^3 hybridized. $\text{Cl}-\text{C}-\text{Cl}$ bond angles are 109.5° . Each $\text{C}-\text{Cl}$ bond is represented by $\sigma: \text{C}(sp^3)^1 - \text{Cl}(3p)^1$

17b. The e^- group geometry around N is trigonal planar, and N is sp^2 hybridized. The $\text{O}-\text{N}-\text{C}$ bond angle is about 120° . The bonds are: $\sigma: \text{O}(2p_y)^1 - \text{N}(sp^2)^1$ $\sigma: \text{N}(sp^2)^1 - \text{Cl}(3p_z)^1$ $\pi: \text{O}(2p_z)^1 - \text{N}(2p_z)^1$.

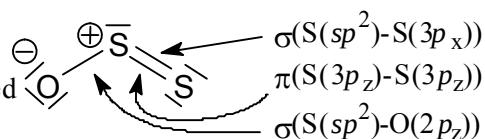
17c. $\text{H}-\text{O}_a-\text{N}=\text{O}_b$. The geometry of O_a is tetrahedral, O_a is sp^3 hybridized and the $\text{H}-\text{O}_a-\text{N}$ bond angle is (at least close to) 109.5° . The e^- group geometry at N is trigonal, N is sp^2 hybridized, and the $\text{O}_a-\text{N}-\text{O}_b$ bond angle is 120° . The four bonds are represented as follows. $\sigma: \text{H}(1s)^1 - \text{O}_a(sp^3)^1$ $\sigma: \text{O}_a(sp^3)^1 - \text{N}(sp^2)^1$ $\sigma: \text{N}(sp^2)^1 - \text{O}_b(2p_y)^1$ $\pi: \text{N}(2p_z)^1 - \text{O}_b(2p_z)^1$.

17d. The e^- group geometry around C is trigonal planar; all bond angles around C are 120° , and the hybridization of C is sp^2 . The four bonds in the molecules are: $2 \times \sigma: \text{Cl}(3p_x)^1 - \text{C}(sp^2)^1$ $\sigma: \text{O}(2p_y)^1 - \text{C}(sp^2)^1$ $\pi: \text{O}(2p_z)^1 - \text{C}(2p_z)^1$.



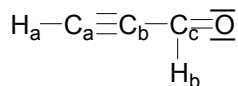
19.

Central S is sp^2 hybridized and the terminal O and S atoms are unhybridized

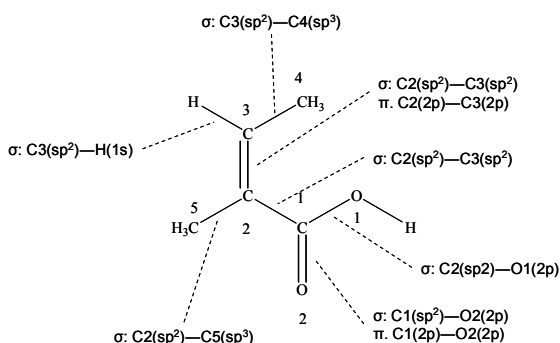
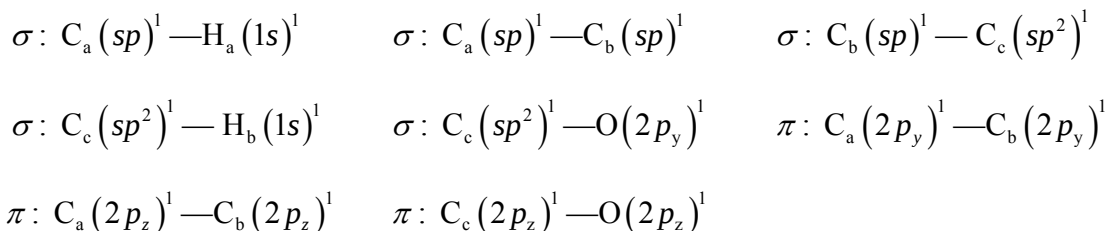


21a.

21b.



23.



25.

. There are 8 atoms that are on the same plane (O1, O2, C1-5, H att. To C3). Furthermore, depending on the angle of rotation of the $-\text{CH}_3$ groups (C4 and C5), two H atoms can also be added to this total.

27. The valence-bond method describes a covalent bond as the result of the overlap of atomic orbitals. Molecular orbital theory describes a bond as a region of space in a molecule where there is a good chance of finding the bonding electrons. The molecular orbital bond does not have to be created from atomic orbitals (although it often is) and the orientations of atomic orbitals do not have to be manipulated to obtain the correct geometric shape. There is little concept of the relative energies of bonding in valence-bond theory. In molecular orbital theory, bonds are ordered energetically.

29. N_2^- bond order = 2.5 (stable), N_2^{2-} bond order = 2 (stable).

31. In order to have a bond order higher than three, there would have to be a region in a molecular orbital diagram where four bonding orbitals occur together in order of increasing energy, with no intervening antibonding orbitals. No such region exists in any of the molecular orbital diagrams in Figure 11-25.

33a. σ_{1s}

33b. σ_{2s}

33c. σ_{1s}^*

33d. σ_{2p}

35a. NO : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*1}$

35b. NO^+ : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4$

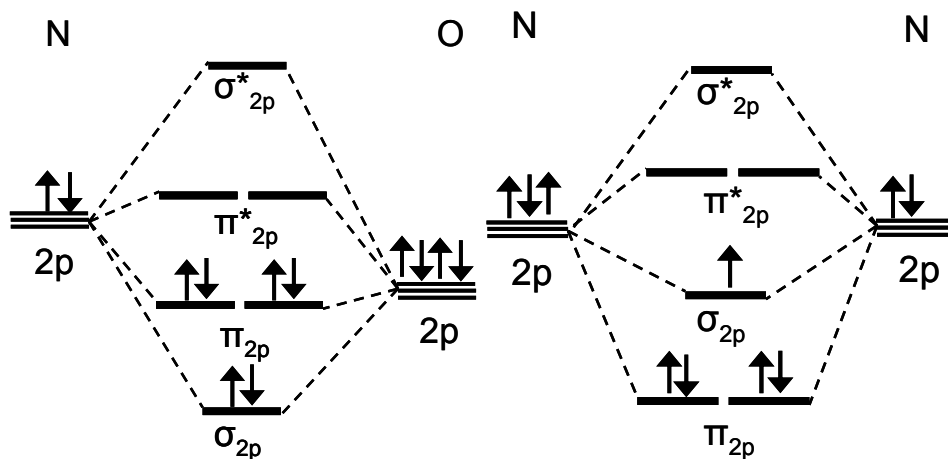
35c. CO : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4$

35d. CN : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^1$

35e. CN^- : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2$

35f. CN^+ : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$

35g. BN : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$

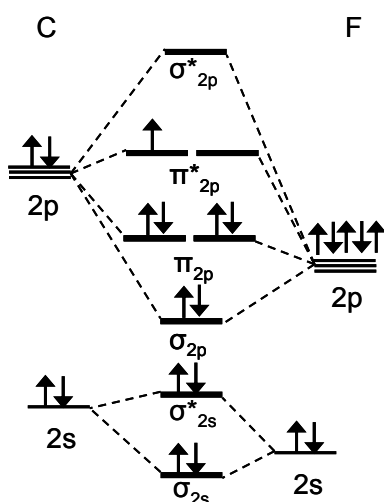


37a.

37b. Bond order is 3 for NO⁺, 2.5 for N₂⁺.

37c. NO⁺ is diamagnetic (all paired electrons), N₂⁺ is paramagnetic.

37d. N₂⁺ has the greater bond length, because there is less electron density between the two nuclei.



39.

. The bond length in CF⁺ would be shorter.

41. The π bonding requires that all six C—C π bonds must be equivalent. This can be achieved by creating six π molecular orbitals—three bonding and three antibonding—into which the 6 π electrons are placed. This creates a single delocalized structure for the C₆H₆ molecule.

43a. Delocalized molecular orbitals required.

43b. Delocalized molecular orbitals required.

43c. Delocalized molecular orbitals not required.

45a. Atomic number, which provides the location of the element in the periodic table, has some minimal predictive value in determining metallic character.

45b. The answer for this part is much the same as the answer to part (a), since atomic mass generally parallels atomic number for the elements.

45c. The number of valence electrons has no bearing on the metallic character of an element.

45d. Because metals occur in every period of the periodic table, there is no particular relationship between the number of electron shells and the metallic behavior of an element.

47. 7.02×10^{20} energy levels, 7.02×10^{20} electrons.

49a. Electrical conductor

49b. Insulator

49c. Insulator

49d. Semiconductor

49e. Electrical conductor

49f. Insulator

51a. No

51b. No

51c. No

51d. Yes

51e. No

51f. Yes

53. In ultra pure crystalline silicon, there are no extra electrons in the lattice that can conduct an electric current. If, however, the silicon becomes contaminated with arsenic atoms, then there will be one additional electron added to the silicon crystal lattice for each arsenic atom that is introduced. The arsenic atoms increase the conductivity of the solid by providing additional electrons that can carry a current after they are promoted into the conduction band by thermal excitation.

55. 1090 nm. This is IR-radiation.

Integrative and Advanced Exercises

58. $[\text{Ne}]_{3s} \uparrow$ The half-filled 3s orbital on each Na overlaps with another to form a σ covalent bond. There are 22 electrons in Na_2 . These electrons are distributed in the molecular orbitals as

follows. $\begin{array}{ccccccc} \sigma_{1s} & \sigma_{1s}^* & \sigma_{2s} & \sigma_{2s}^* & \sigma_{2p} & \pi_{2p} & \pi_{2p}^* & \sigma_{2p}^* & \sigma_{3s} \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} \end{array}$ Again, we predict a single bond for Na_2 . A Lewis-theory picture of the bonding would have the two Lewis symbols for two Na atoms uniting to form a bond: $\text{Na} \cdot \cdot \text{Na} \longrightarrow \text{Na} - \text{Na}$ Thus, the bonding in Na_2 is very much like that in H_2 .

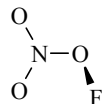
60a. O_2^- $\begin{array}{ccccccc} \sigma_{1s} & \sigma_{1s}^* & \sigma_{2s} & \sigma_{2s}^* & \sigma_{2p} & \pi_{2p} & \pi_{2p}^* & \sigma_{2p}^* \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} \end{array}$, bond order = 1.5.

O_2^{2-} $\begin{array}{ccccccc} \sigma_{1s} & \sigma_{1s}^* & \sigma_{2s} & \sigma_{2s}^* & \sigma_{2p} & \pi_{2p} & \pi_{2p}^* & \sigma_{2p}^* \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} \end{array}$, bond order = 1.0.

60b. O_2^- $[\text{O}=\text{O}\cdot]^-$, O_2^{2-} $[\text{O}=\text{O}]^{2-}$

64. $\begin{array}{c} \text{O} \\ | \\ \text{F}-\text{O}_a-\text{N}-\text{O} \\ || \\ \text{O} \end{array} \longleftrightarrow \begin{array}{c} \text{O} \\ | \\ \text{F}-\text{O}_a-\text{N}=\text{O} \\ | \\ \text{O} \end{array}$

$\sigma: \text{F}(2p) - \text{O}_a(sp^3)$ $\sigma: \text{O}_a(sp^3) - \text{N}(sp^2)$ $\sigma: \text{N}(sp^2) - \text{O}(2p_y)$ $\pi: \text{N}(2p_z) - \text{O}(2p_z)$



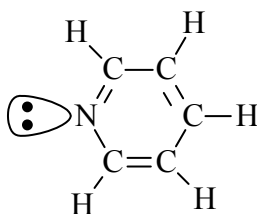
66a. For ClF_3 the electron group geometry is trigonal bipyramidal and the molecule is T-shaped. For AsF_5 the electron group geometry and molecular shape are trigonal bipyramidal. For ClF_2^+ the electron group geometry is tetrahedral and the ion is bent in shape. For AsF_6^- the electron group geometry and the shape of this ion are octahedral.

66b. Trigonal bipyramidal electron group geometry is associated with sp^3d hybridization. The Cl in ClF_3 and As in AsF_5 both have sp^3d hybridization. Tetrahedral electron group geometry is associated with sp^3 hybridization. Thus Cl in ClF_2^+ has sp^3 hybridization. Octahedral electron group geometry is associated with sp^3d^2 hybridization, which is the hybridization adopted by As in AsF_6^- .

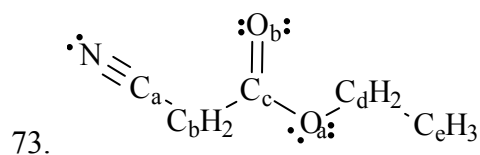
68. Suppose two He atoms in the excited state $1s^1 2s^1$ unite to form an He_2 molecule. One possible configuration is $\sigma_{1s}^2 \sigma_{1s}^{*0} \sigma_{2s}^2 \sigma_{2s}^{*0}$. The bond order would be $(4-0)/2 = 2$.

70. The orbital diagrams for C and N are as follows. C $[\text{He}] sp^2 \boxed{\uparrow\uparrow\uparrow} 2p \boxed{\uparrow}$, N $[\text{He}] sp^2 \boxed{\uparrow\uparrow\uparrow} 2p \boxed{\uparrow}$

antibonding π molecular orbitals $\left\{ \begin{array}{c} \boxed{} \\ \boxed{} \end{array} \right.$
bonding π molecular orbitals $\left\{ \begin{array}{c} \boxed{\uparrow\downarrow} \\ \boxed{\uparrow\downarrow} \end{array} \right.$



Number of π -bonds = 3
This π -bonding scheme produces three π -bonds, which is identical to the number predicted by Lewis theory.



C_b-H , C_d-H , C_e-H : σ $H(1s) - C(sp^3)$ (all tetrahedral carbon uses sp^3 hybrid orbitals)

$C_c=O_b$: σ $C_c(sp^2) - O_b(2p \text{ or } sp^2)$, π : $C_c(2p) - O_b(2p)$

C_c-O_a : σ $C_c(sp^2) - O_a(2p \text{ or } sp^3)$

C_d-O_a : σ $C_d(sp^3) - O_a(2p \text{ or } sp^3)$

$C_a \equiv N$: σ $C_a(sp) - N(sp)$

Two mutually perpendicular π -bonds: $C(2p) - N(2p)$

C_a-C_b : σ $C_b(sp^3) - C_a(sp)$

C_d-C_e : σ $C_d(sp^3) - C_e(sp^3)$

C_c-C_b : σ $C_b(sp^3) - C_c(sp^2)$

75a. 4.00 watts

75b. 8.9 amps

79. The wavelength for both will be the same, because they both have a conjugated π system.

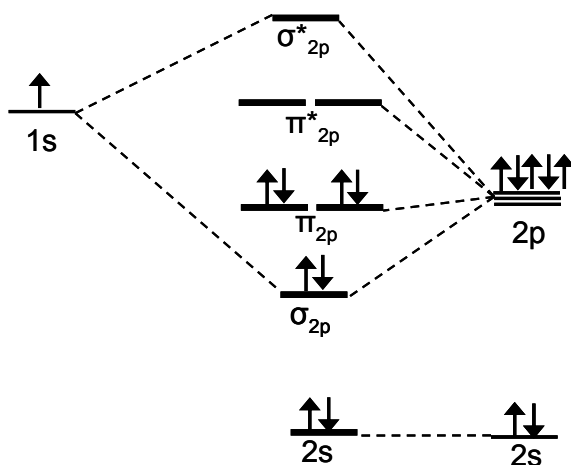
Feature Problems

80a. -205.4 kJ

80b. -117.9 kJ

80c. -148.3 kJ

80d. $\Delta H^\circ_{\text{atomization}} = 5358 \text{ kJ (per mole of } C_6H_6)$, Resonance energy = -168 kJ.



87.

Self-Assessment Exercises

91. The answer is (c).

92. The answer is (c).

93. The answer is (a).

94. The answer is (b).

95. The answer is (c).

96. The answer is (d).

97. The answer is (a).

98. The answer is (c).

99. The valence-bond method using pure s and p orbitals incorrectly predicts a trigonal pyramidal shape with 90° F—B—F bond angles.

100. BrF_5 has six constituents around it; five are fluorine atoms, and the sixth is a lone pair. Therefore, the hybridization is sp^3d^2 , but the geometry is square pyramidal.

101. There are (a) 6 σ and (b) 2 π bonds.

102. All three are paramagnetic. B_2^- has 3 bonding electrons, so the B—B bond is the strongest.

103. The answer is (c).

104. C_2^+

105. C_2 has the greater bond energy.

Chapter 12 Answers

Practice Examples

1a. CH_3CN is polar and thus has the strongest intermolecular forces and should have the highest boiling point.

1b. $(\text{CH}_3)_3\text{CH} < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 < \text{SO}_3 < \text{C}_8\text{H}_{18} < \text{C}_6\text{H}_5\text{CHO}$

2a. 0.923 kJ

2b. -1025 J

3a. 151 Torr

3b. $\approx 1.7 \text{ g/L}$

4a. Vapor only

4b. 0.0435 g H_2O vapor, 0.089 g liquid water .

5a. 121 mmHg

5b. 42.9 mmHg

6a. He , Ne, O_2 , O_3 , Cl_2 , $(\text{CH}_3)_2\text{CO}$.

6b. The magnitude of the enthalpy of vaporization is strongly related to the strength of intermolecular forces: the stronger these forces, the more endothermic the vaporization process. The first three substances all are nonpolar and, therefore, their only intermolecular forces are London forces, whose strength primarily depends on molar mass. The substances are arranged in order of increasing molar mass: $\text{H}_2 = 2.0 \text{ g/mol}$, $\text{CH}_4 = 16.0 \text{ g/mol}$, $\text{C}_6\text{H}_6 = 78.1 \text{ g/mol}$, and also in order of increasing heat of vaporization. The last substance has a molar mass of 61.0 g/mol, which would produce intermolecular forces smaller than those of C_6H_6 if CH_3NO_2 were nonpolar. But the molecule is definitely polar. Thus, the strong dipole–dipole forces developed between CH_3NO_2 molecules make the enthalpy of vaporization for CH_3NO_2 larger than that for C_6H_6 , which is, of course, essentially non-polar.

7a. Moving from point R to P we begin with $\text{H}_2\text{O}(\text{g})$ at high temperature ($>100^\circ\text{C}$). When the temperature reaches the point on the vaporization curve, OC, water condenses at constant temperature (100°C). Once all of the water is in the liquid state, the temperature drops. When the temperature reaches the point on the fusion curve, OD, ice begins to form at constant temperature (0°C). Once all of the water has been converted to $\text{H}_2\text{O}(\text{s})$, the temperature of the sample decreases slightly until point P is reached.

Since solids are not very compressible, very little change occurs until the pressure reaches the point on the fusion curve OD. Here, melting begins. A significant decrease in the volume occurs ($\approx 10\%$) as ice is converted to liquid water. After melting, additional pressure produces very little change in volume because liquids are not very compressible.

51.3 L
At
Point
R

7b. 15.3 L
at 100°C
1/2 vap

8a. Lower melting point than KI: RbI or CsI. Melting point higher than CaO: MgO, Ga_2O_3 , Ca_3N_2 , Mg_3N_2 .

8b. NaI

9a. 524 pm

9b. $6.628 \times 10^7 \text{ pm}^3$

10a. 0.86 g/cm^3

10b. $6.035 \times 10^{23} \frac{\text{atoms Al}}{\text{mol Al}}$

11a. 402 pm

11b. 2.21 g/cm^3

12a. -669.2 kJ/mol

12b. -764 kJ/mol

Integrative Example

A. At 25.0°C , the vapor pressure of water is 23.8 mmHg. The vapor pressure for isooctane (using the Clausius-Clapeyron equation) is 43.1 mm Hg, higher than H_2O 's vapor pressure.

B. $E_{\text{A}_2} = +881 \text{ kJ}$.

Exercises

1a. London forces between HCl molecules are expected to be relatively weak; Hydrogen bonding is weak ; No hydrogen bonds; Dipole–dipole interactions should be relatively strong.

1b. Neither hydrogen bonds nor dipole–dipole attractions can occur; London forces are more important.

1c. No hydrogen bonds; London forces are as strong; Dipole–dipole interactions are important.

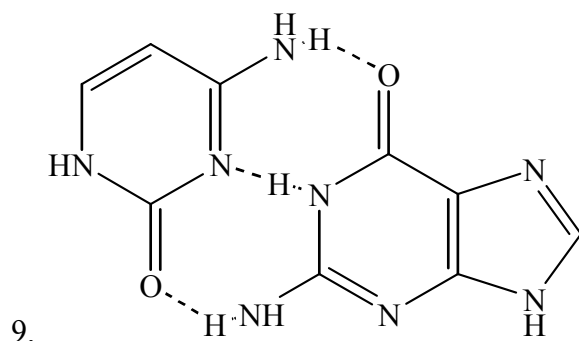
1d. London forces are not very important; Hydrogen bonding is most important interaction between HF molecules.

1e. H bonds are not important; There are no dipole-dipole interactions; London forces are quite weak.

3. (c) < (b) < (d) < (a).

5. CH₃OH

7. Three water molecules.



11. Since both the silicone oil and the cloth or leather are composed of relatively nonpolar molecules, they attract each other. Water, on the other hand is polar and adheres very poorly to the silicone oil (actually, the water is repelled by the oil), much more poorly, in fact, than it adheres to the cloth or leather. This is because the oil is more nonpolar than is the cloth or the leather. Thus, water is repelled from the silicone-treated cloth or leather.

13. Molasses, like honey, is a very viscous liquid (high resistance to flow). The coldest temperatures are generally in January (in the northern hemisphere). Viscosity generally increases as the temperature decreases. Hence, molasses at low temperature is a very slow flowing liquid. Thus there is indeed a scientific basis for the expression “slower than molasses in January.”

15. CCl₄ < CH₃CH₂OCH₂CH₃ < CH₃OH

17. The intermolecular interactions in butanol are dominated by H-bonding, which is much stronger than the London dispersion forces dominant in pentane.

19. The process of evaporation is endothermic, meaning it requires energy. If evaporation occurs from an uninsulated container, this energy is obtained from the surroundings, through the walls of the container. However, if the evaporation occurs from an insulated container, the only source of the needed energy is the liquid that is evaporating. Therefore, the temperature of the liquid will decrease as the liquid evaporates.

21. 8.88 L $C_6H_6(l)$

23. 40.5 kJ

25. 221 L methane

27a. 45 mmHg

27b. 110°C

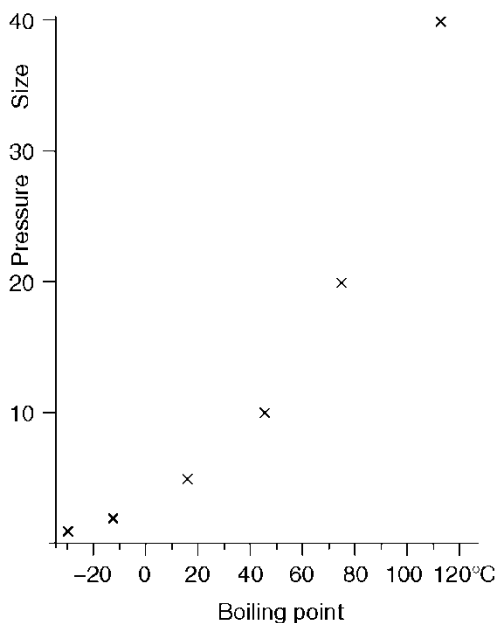
29. 226 mmHg

31a. In order to vaporize water in the outer container, heat must be applied (i.e., vaporization is an endothermic process). When this vapor (steam) condenses on the outside walls of the inner container, that same heat is liberated. Thus condensation is an exothermic process.

31b. 100.00° C

33. 120.7° C

35. 0.907 mmHg



37. , 6.5 atm.

39. 49.7 kJ/mol

41. 33° C

43. 0.0981 atm

45. Substances that can exist as a liquid at room temperature (about 20° C) have critical temperature above 20° C, 293 K. Of the substances listed in Table 12.5, CO₂, HCl, NH₃, SO₂, and H₂O can exist in liquid form at 20 °C.

47a. -776 kJ

47b. 2.5×10^4 kJ

49. Liquid and gas.

51a. The upper-right region of the phase diagram is the liquid region, while the lower-right region is the region of gas.

51b. As the phase diagram shows, the lowest pressure at which liquid exists is at the triple point pressure, namely, 43 atm. 1.00 atm is far below 43 atm. Thus, liquid cannot exist at this pressure, and solid sublimates to gas instead.

51c. As we move from point *A* to point *B* by lowering the pressure, initially nothing happens. At a certain pressure, the solid liquefies. The pressure continues to drop, with the entire sample being liquid while it does, until another, lower pressure is reached. At this lower pressure the entire sample vaporizes. The pressure then continues to drop, with the gas becoming less dense as the pressure falls, until point *B* is reached.

53a. 0.0418 atm

53b. 0.110 atm

53c. 0.117 atm

55a. No

55b. No

55c. Yes

55d. Possible, yes.

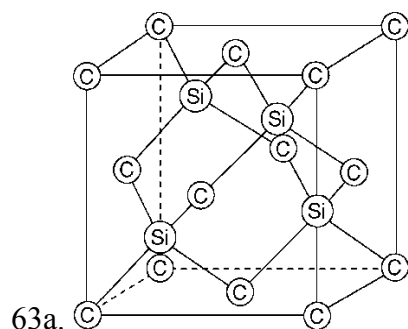
55e. No

57a. 0.22 kg

57b. 27 g steam

59. The liquid in the can is supercooled. When the can is opened, gas bubbles released from the carbonated beverage serve as sites for the formation of ice crystals. The condition of supercooling is destroyed and the liquid reverts to the solid phase. An alternative explanation follows. The process of the gas coming out of solution is endothermic (heat is required). The required heat is taken from the cooled liquid, causing it to freeze.

61. Diamond

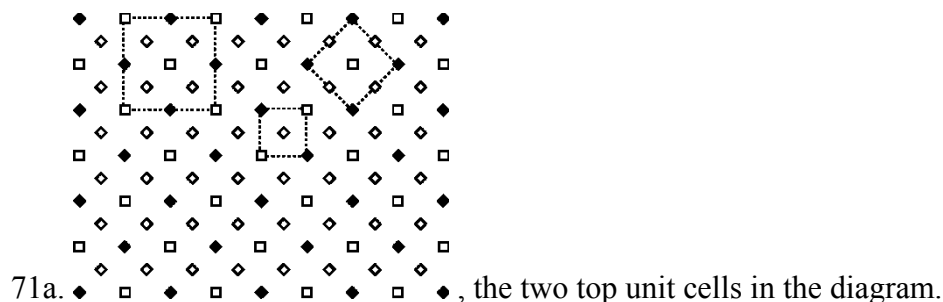


63b. sp^2 hybridization for each atom. The half-filled sp^2 hybrid orbitals of the boron and nitrogen atoms overlap to form the σ bonding structure, and a hexagonal array of atoms. The $2p_z$ orbitals then overlap to form the π bonding orbitals.

65. We expect forces in ionic compounds to increase as the sizes of ions become smaller and as ionic charges become greater. As the forces between ions become stronger, a higher temperature is required to melt the crystal. In the series of compounds NaF, NaCl, NaBr, and NaI, the anions are progressively larger, and thus the ionic forces become weaker. We expect the melting points to decrease in this series from NaF to NaI.

67. NaF

69. In each layer of a closest packing arrangement of spheres, there are six spheres surrounding and touching any given sphere. A second similar layer then is placed on top of this first layer so that its spheres fit into the indentations in the layer below. The two different closest packing arrangements arise from two different ways of placing the third layer on top of these two, with its spheres fitting into the indentations of the layer below. In one case, one can look down into these indentations and see a sphere of the bottom (first) layer. In the other case, no first layer sphere is visible through the indentation.



71b. The unit cell has one light-colored square per unit cell, 2 circles per unit cell, 1 diamond per unit cell.

71c. The small square outlined near the center of the figure drawn in part (a).

73. 19.25 g/cm^3

75a. 335 pm

75b. 9.23 g cm^{-3}

75c. 15.45°

77. 2 Si atoms per unit cell.

79. CaF_2 : There are eight Ca^{2+} ions on the corners for a total of one corner ion per unit cell. There are six Ca^{2+} ions on the faces for a total of three face ions per unit cell. This gives a total of four Ca^{2+} ions per unit cell. There are eight F^- ions, each wholly contained within the unit cell. The ratio of Ca^{2+} ions to F^- ions is 4 Ca^{2+} ions per 8 F^- ions: Ca_4F_8 or CaF_2 . TiO_2 .

There are eight Ti^{4+} ions on the corners for a total of one Ti^{4+} corner ion per unit cell. There is one Ti^{4+} ion in the center, wholly contained within the unit cell. Thus, there are a total of two Ti^{4+} ions per unit cell. There are four O^{2-} ions on the faces of the unit cell, each shared between two unit cells, for a total of two face atoms per unit cells. There are two O^{2-} ions totally contained within the unit cell. This gives a total of four O^{2-} ions per unit cell. The ratio of Ti^{4+} ions to O^{2-} ions is 2 Ti^{4+} ions per 4 O^{2-} ion: Ti_2O_4 or TiO_2 .

81a. The coordination number of Mg^{2+} is 6 and that of O^{2-} is 6 also.

81b. Four formula units per unit cell of MgO .

81c. Length = 424 pm, volume = $7.62 \times 10^{-23} \text{ cm}^3$.

81d. 3.51 g/cm^3

83a. Face centered cubic

83b. Face centered cubic

83c. Face centered cubic

85. Lattice energies of a series such as LiCl(s) , NaCl(s) , KCl(s) , RbCl(s) , and CsCl(s) will vary approximately with the size of the cation. A smaller cation will produce a more exothermic lattice energy. Thus, the lattice energy for LiCl(s) should be the most exothermic and CsCl(s) the least in this series, with NaCl(s) falling in the middle of the series.

87. -645 kJ/mol. MgCl_2 is much more stable than MgCl , since considerably more energy is released when it forms.

Integrative and Advanced Exercises

91. In many instances, the substance in the tank is not present as a gas only, but as a liquid in equilibrium with its vapor. As gas is released from the tank, the liquid will vaporize to replace it, maintaining a pressure in the tank equal to the vapor pressure of the substance at the temperature at which the cylinder is stored. This will continue until all of the liquid vaporizes, after which only gas will be present. The remaining gas will be quickly consumed, and hence the reason for the warning. However, the situation of gas in equilibrium with liquid only applies to substances that have a critical temperature above room temperature (20 °C or 293 K).

93. At 100°C, the quantity of heat needed is 2257 J/g H₂O. Thus, less heat is needed to vaporize 1.000 g of H₂O at the higher temperature of 100. °C. This makes sense, for at the higher temperature the molecules of the liquid already are in rapid motion. Some of this energy of motion or vibration will contribute to the energy needed to break the cohesive forces and vaporize the molecules.

96. The final condition is a point on the vapor pressure curve at 30.0 °C.

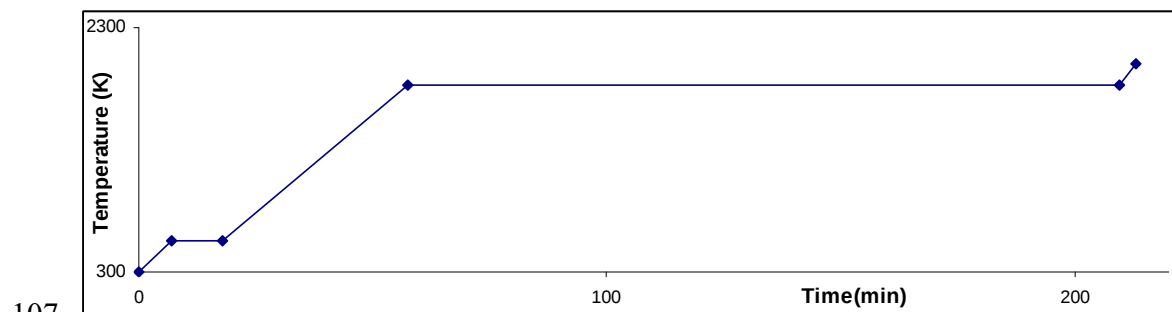
99a. 31 atm

99b. -0.25 °C

100. 87 °C

103. 54.3% dimer . We would expect the % dimer to decrease with temperature.

104. 1.84 kg N₂



109. 16.0°

Feature Problems

119. 0.021 J/m²

$$120a. \ln\left(\frac{P_2}{P_1}\right) = \frac{(15,971)}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{(14.55)}{R} \ln\left(\frac{T_2}{T_1}\right) - \frac{(0.160)}{R} (T_2 - T_1)$$

120b. 169 K

Self-Assessment Exercises

128. The answer is (c).

129. The answer is (c).

130. The answer is (b).

131. The answer is (a).

132. The answers are (d) and (f).

133a. $C_{10}H_{22}$

133b. $(CH_3)_2O$

133c. CH_3CH_2OH

134. O_3 is out of place. The correct order of boiling points based on molar masses is: $N_2 < F_2 < Ar < O_3 < Cl_2$.

135. $Ne < C_3H_8 < CH_3CH_2OH < CH_2OHCHOHCH_2OH < KI < K_2SO_4 < MgO$

136. Refer to the photograph on page 518 of water boiling under a reduced pressure. If the vapor is evacuated fast enough, to supply the required ΔH_{vap} , the water may cool to $0^\circ C$ and ice may begin to form.

137. If there is too little benzene(l) in the sealed tube in Figure 12-22 initially, the liquid will all be converted to benzene(g) before T_c is reached. If too much is present initially, the liquid will expand and cause the benzene(l) to condense, and therefore only benzene(l) will be present at the time T_c is reached.

138a. All the CCl_4 will be in the vapor phase.

138b. 666 kJ

139a. 362 pm

139b. $4.74 \times 10^7 \text{ pm}^3$

139c. 4 atoms/unit cell.

139d. 74%

139e. $4.221 \times 10^{-22} \text{ g}$

139f. 8.91 g/cm^3

140. The answer is (a).

141. The answer is (d).

142. A network covalent solid will have a higher melting point, because it takes much more energy to overcome the covalent bonds in the solid (such as, for example, diamond) than to overcome ionic interactions.

143. 2.13 Å

144. The answer is (c).

Chapter 13 Answers

Practice Examples

1a. 16.2% ethanol by mass

1b. (a) 0.927 ; (b) 3.73 M ; (c) 4.34 m .

2a. 0.03593

2b. (a) 0.3038 M ; (b) 0.3246 m ; (c) 0.005815 .

3a. Oxalic acid should be the most readily soluble in water because it is polar and can form hydrogen bonds.

3b. I_2 should dissolve well in CCl_4 by simple mixing.

4a. Suggestion 1: 31 g NH_4Cl crystallized ; Suggestion 2: 46 g of NH_4Cl crystallized.

4b. KNO_3 (47%) > $KClO_4$ (38%) > K_2SO_4 (21%)

5a. 0.717 atm O_2 pressure

5b. 6.328 atm

6a. $P_{hex} = 112$ mmHg ; $P_{pen} = 127$ mmHg ; $P_{tot} = 239$ mmHg.

6b. $P_{tol} = 13.0$ mmHg ; $P_{benz} = 51.5$ mmHg ; $P_{tot} = 64.5$ mmHg.

7a. $y_{hexane} = 0.469$, $y_{pentane} = 0.531$.

7b. $y_t = 0.202$, $y_b = 0.798$.

8a. 0.857 atm

8b. 8.24×10^{-3} g

9a. 8.60×10^4 g/mol

9b. 0.0105 atm

10a. (a) 0.122 m ; (b) 377 g/mol ; (c) $C_{17}H_{20}O_6N_4$.

10b. Lower than 760.0 mmHg.

11a. 3.89 atm

11b. 0.560 mL conc soln

Integrative Example

A. 29.3% H_2O , $\chi_{\text{phenol}} = 0.161$.

B. (a) 0.48 mmHg; (b) 0.42 mmHg.

Exercises

1. $\text{NH}_2\text{OH}(\text{s})$ should be the most soluble.

3. Salicyl alcohol probably is moderately soluble in both benzene and water. The reason for this assertion is that salicyl alcohol contains a benzene ring, which would make it soluble in benzene, and also can use its $-\text{OH}$ groups to hydrogen bond to water molecules.

5. (c) Formic acid and (f) propylene glycol are soluble in water. (b) Benzoic acid and (d) 1-Butanol are only slightly soluble in water. (a) Iodoform and (e) chlorobenzene are insoluble in water.

7. KF is probably the most water soluble, based on smallest lattice energy.

9. 53.7 g NaBr/100 g solution.

11. 1.83×10^4 L sol'n

13. For water, the mass in grams and the volume in mL are about equal; the density of water is close to 1.0 g/mL. For ethanol, on the other hand, the density is about 0.8 g/mL. As long as the final solution volume after mixing is close to the sum of the volumes for the two pure liquids, the percent by volume of ethanol will have to be larger than its percent by mass. This would not necessarily be true of other ethanol solutions. It would only be true in those cases where the density of the other component is greater than the density of ethanol.

15. 21.6 g $\text{HC}_2\text{H}_3\text{O}_2$

17. 4.80×10^{-4} M

19. 1.85 M

21. 113 mL conc. soln

23. 0.00654 M

25. 0.410 *m*

27. 54.8 g I_2

29. 4.19 M, 5.26 *m*.

31a. $\chi_{\text{C}_7\text{H}_{16}} = .187$, $\chi_{\text{C}_8\text{H}_{18}} = 0.427$, $\chi_{\text{C}_9\text{H}_{20}} = 0.386$.

31b. 18.7 mol% C_7H_{16} , 42.7 mol% C_8H_{18} , 38.6 mol% C_9H_{20} .

33a. 0.00204

33b. 0.0101

35. 207 mL glycerol

37. 4.36×10^{16} atoms, $\chi_{pb} = 1.303 \times 10^{-6}$.

39. 8.66 m

41a. Unsaturated

41b. 3.0 g $KClO_4$

43. 4.48×10^{-3} M

45. 4×10^2 g CH_4 (natural gas)

47. 1.40×10^{-5} M

49. Because of the low density of molecules in the gaseous state, the solution volume remains essentially constant as a gas dissolves in a liquid. Changes in concentrations in the solution result from changes in the number of dissolved gas molecules. This number is directly proportional to the mass of dissolved gas.

51. $P_b = 40.6$ mmHg, $P_t = 16.3$ mmHg, $P_{tot} = 56.9$ mmHg

53. $P_{sol'n} = 23.2$ mmHg

55. $y_e = 0.68$, $y_s = 0.32$.

57. 1.29×10^3 mmHg

59. 3.2×10^4 g/mol

61. Both the flowers and the cucumber contain ionic solutions (plant sap), but both of these solutions are less concentrated than the salt solution. Thus, the solution in the plant material moves across the semipermeable membrane in an attempt to dilute the salt solution, leaving behind wilted flowers and shriveled pickles (wilted/shriveled plants have less water in their tissues).

63. ≈ 22.4 L solvent

65. 2.8×10^5 g/mol

67. 21 atm

69. 1.2×10^2 g/mol

71a. $20.^\circ\text{C}/m$

71b. Cyclohexane is the better solvent for freezing-point depression determinations of molar mass, because a less concentrated solution will still give a substantial freezing-point depression.

73. $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$

75. $\text{C}_4\text{H}_4\text{S}$

77. 120 g NaCl, No.

79. 1.04

81a. -0.186°C

81b. -0.372°C

81c. -0.372°C

81d. -0.558°C

81e. -0.372°C

81f. -0.186°C

81g. $< -0.186^\circ\text{C}$

83. The combination of $\text{NH}_3(\text{aq})$ with $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$, results in the formation of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2(\text{aq})$, which is a solution of the ions NH_4^+ and CH_3COO^- . This solution of ions or strong electrolytes conducts a current very well.

85. The answer is (d).

Integrative and Advanced Exercises

88. 682 g H_2O

92. 4.5 kg H_2O

95. 1×10^1 % palmitic acid

97. $\chi_{\text{urea}} = \chi_{\text{sucrose}} = 0.00161$, mole fraction of water = 0.99839.

100a. $1.56 \times 10^{-3} \text{ m}^2$

100b. $8.34 \times 10^{-7} \text{ m}^2$

105. Volume % N_2 = 65.38% , volume % O_2 = 34.62%.

107. 1.3×10^2 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

109. 0.0125 g / L, 0.73 atm .

111. 5.96 L

Feature Problems

114a. $\chi_{\text{HCl}} > 0.50$

114b. The composition of $\text{HCl}(\text{aq})$ changes as the solution boils in an open container because the vapor has a different composition than does the liquid. Thus, the component with the lower boiling point is depleted as the solution boils. The boiling point of the remaining solution must change as the vapor escapes due to changing composition.

114c. The azeotrope occurs at the maximum of the curve: at $\chi_{\text{HCl}} = 0.12$ and a boiling temperature of 110°C .

114d. $\chi_{\text{HCl}} = 0.112$

115a. 90.04%

115b. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ deliquesces if the relative humidity is over 32%. Thus, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ will deliquesce.

115c. If the substance in the bottom of the desiccator has high water solubility, its saturated solution will have a low χ_{water} , which in turn will produce a low relative humidity.

116a. Using 0.92% $\text{NaCl}(\text{aq})$ and $i = 2.0$ gives $\Delta T_f = -0.60^\circ\text{C}$, fair agreement with -0.52°C .

116b. $\Delta T_f = -0.60^\circ\text{C}$, close to the defined freezing point of -0.52°C .

Self-Assessment Exercises

120. The answer is (b).

121. The answer is (d).

122. The answer is (a).

123. The answer is (d).

124. The answer is (c).

125. Unsaturated

126a. 0.16 M Na^+

126b. 0.32 M

126c. 8.1 atm

126d. $-0.60\text{ }^{\circ}\text{C}$

127a. 7.80 M $\text{C}_3\text{H}_8\text{O}_3$

127b. 24.4 M H_2O

127c. 34.0 *m* H_2O

127d. 0.242

127e. 75.8%

128. 1-b, 2-d, 3-d, 4-a.

130. The answer is (b).

131. The magnitude of $\Delta H_{\text{lattice}}$ is larger than the sum of the $\Delta H_{\text{hydration}}$ of the individual ions.

132. The answer is (a).

133. The answer is (b).

134. The answer is (a).

135. The answer is (e).

136. The answer is (c).

Chapter 14 Answers

Practice Examples

1a. $4.46 \times 10^{-5} \text{ M s}^{-1}$

1b. $1.62 \times 10^{-4} \text{ M s}^{-1}$

2a. (a) $3.3 \times 10^{-4} \text{ M s}^{-1}$; (b) 0.37 M .

2b. 2.17 M . This value differs from the value of 2.15 M determined in *text* Example 14-2b because the *text* used the initial rate of reaction, which is a bit faster than the average rate over the first 400 seconds.

3a. First-order

3b. $3.9 \times 10^{-7} \text{ M min}^{-1}$

4a. $4.4 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$

4b. $2.4 \times 10^{-7} \text{ M min}^{-1}$

5a. 1.0 M

5b. Substitute the provided values into *text* Equation 14.13. The two k values agree within the limits of the experimental error and thus, the reaction is first-order in $[\text{H}_2\text{O}_2]$.

6a. 64.2%

6b. 25.1 min

7a. 272 mmHg

7b. (a) $1.9 \times 10^{-7} \text{ mmHg}$; (b) $1.56 \times 10^3 \text{ mmHg}$.

8a. First-order, $k = 6.93 \times 10^{-3} \text{ s}^{-1}$.

8b. Zero-order, $k = 9.28 \times 10^{-3} \text{ M / min}$.

9a. 43 s

9b. 311 K

10a. The first step is the slow step. Rate of reaction = $k_1 [\text{NO}_2]^2$.

10b. (1) The steps of the mechanism add to produce the overall reaction. (2) The predicted rate law, $\text{Rate} = (k_1 k_3 / k_2) [\text{NO}_2] [\text{F}_2]$, agrees with the experimental rate law.

Integrative Example

A. (a) 44 kJ/mol; (b) 20. h.

B. The rate of reaction is: $\text{Rate} = k_2[A^*] = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$. At low pressures ($[A] \sim 0$ and

hence $k_2 \gg k_{-1}[A]$), the denominator becomes $\sim k_2$ and the rate law is

$\text{Rate} = \frac{k_2 k_1 [A]^2}{k_2} = k_1 [A]^2$. Second-order with respect to $[A]$. At high pressures ($[A]$ is large

and $k_{-1}[A] \gg k_2$), the denominator becomes $\sim k_{-1}[A]$ and the rate law

is $\text{Rate} = \frac{k_2 k_1 [A]^2}{k_{-1}[A]} = \frac{k_2 k_1 [A]}{k_{-1}}$. First-order with respect to $[A]$.

Exercises

1a. $3.1 \times 10^{-4} \text{ Ms}^{-1}$

1b. $3.1 \times 10^{-4} \text{ Ms}^{-1}$

1c. $9.3 \times 10^{-4} \text{ Ms}^{-1}$

3. $1.0 \times 10^{-3} \text{ M s}^{-1}$

5a. 0.575 M

5b. 5.4 min

7a. $3.52 \times 10^{-5} \text{ M/s}$

7b. 0.357 M

7c. $4.5 \times 10^2 \text{ s}$

9a. 3000. mmHg

9b. 1400. mmHg

11a. First-order with respect to A, second-order with respect to B.

11b. Third-order overall.

11c. $0.102 \text{ M}^{-2} \text{ s}^{-1}$

13. $\text{Rate} = k [\text{NO}]^2 [\text{Cl}_2]$, $k = 5.70 \text{ M}^{-2} \text{ s}^{-1}$.

15a. True

15b. False

17a. 3.13%

17b. 0.00193 M/s

19a. 19 min

19b. 0.18 g A

21. 20.6 min

23a. 218 min

23b. 2.3 L CO₂

25a. The virtual constancy of the rate constant throughout the time of the reaction confirms that the reaction is first-order.

25b. $1.86 \times 10^{-3} \text{ s}^{-1}$

25c. 0.148 M

27a. Set II

27b. Set I

27c. Set III

29. 70 s

31a. 0.010 M s^{-1}

31b. 0.0048 M s^{-1}

31c. 0.0034 M s^{-1}

33. $1.39 \times 10^{-4} \text{ M / min}$

35. The reaction is second-order in HI at 700 K. $\text{Rate} = k[\text{HI}]^2$. $k = 0.00118 \text{ M}^{-1}\text{s}^{-1}$.

37a. Zero-order

37b. 72 s

39a. $+0.022 \text{ M / min}$, $+0.089 \text{ M / min}$.

39b. Second-order

41. $\text{Rate} = k[\text{A}]^2$ and $k = 0.020 \text{ L mol}^{-1}\text{min}^{-1}$.

43. A zero-order reaction has a half life that varies proportionally to $[\text{A}]_0$, therefore, increasing $[\text{A}]_0$ increases the half-life for the reaction. A second-order reaction's half-life varies inversely proportional to $[\text{A}]_0$, that is, as $[\text{A}]_0$ increases, the half-life decreases. The reason for the

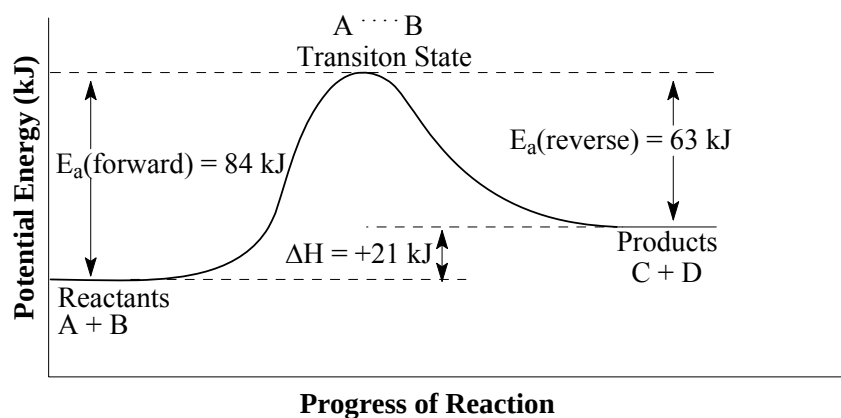
difference is that a zero-order reaction has a constant rate of reaction (independent of $[A]_0$). In a second-order reaction, the rate of reaction increases as the square of the $[A]_0$.

45a. The rate of a reaction depends on at least two factors other than the frequency of collisions. The first of these is whether each collision possesses sufficient energy to get over the energy barrier to products. The second factor is whether the molecules in a given collision are properly oriented for a successful reaction.

45b. Although the collision frequency increases relatively slowly with temperature, the fraction of those collisions that have sufficient energy to overcome the activation energy increases much more rapidly. Therefore, the rate of reaction will increase dramatically with temperature.

45c. The addition of a catalyst has the net effect of decreasing the activation energy of the overall reaction, by enabling an alternative mechanism. The lower activation energy of the alternative mechanism means that a larger fraction of molecules have sufficient energy to react. Thus the rate increases, even though the temperature does not.

47a. 63 kJ/mol



47b.

49a. Two

49b. Three

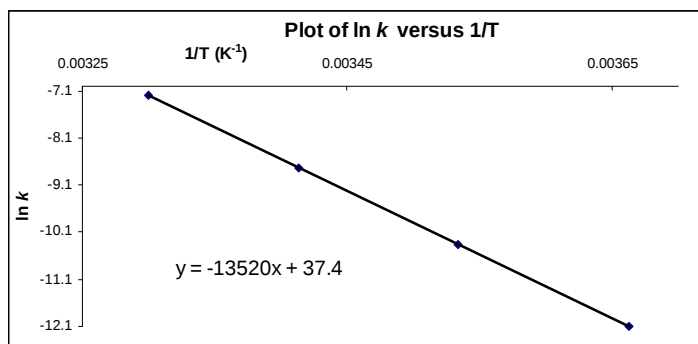
49c. Step 3

49d. Step 1

49e. Endothermic

49f. Exothermic

51. 160 kJ/mol



53a.

53b. 112 kJ mol^{-1}

53c. $2.3 \times 10^2 \text{ s}$

55a. 34.8 kJ/mol

55b. 61°C

57a. 51 kJ/mol

57b. Since the activation energy for the depicted reaction is 209 kJ/mol , we would not expect this reaction to follow the rule of thumb.

59a. Although a catalyst is *recovered unchanged from the reaction mixture*, it does “take part in the reaction.” Some catalysts actually slow down the rate of a reaction. Usually, however, these negative catalysts are called inhibitors.

59b. The function of a catalyst is to *change the mechanism of a reaction*. The new mechanism is one that has a different (lower) activation energy (and frequently a different A value), than the original reaction.

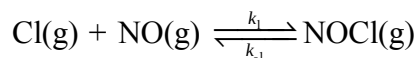
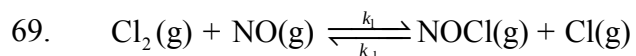
61. Both platinum and an enzyme have a metal center that acts as the active site. Generally speaking, platinum is not dissolved in the reaction solution (heterogeneous), whereas enzymes are generally soluble in the reaction media (homogeneous). Platinum is rather nonspecific, catalyzing many different reactions. An enzyme is quite specific, usually catalyzing only one reaction rather than all reactions of a given class.

63. An excess of substrate must be present.

65. The molecularity is equal to the order of the overall reaction only if the elementary process in question is the slowest and, thus, the rate-determining step of the overall reaction. In addition, the elementary process in question should be the only elementary step that influences the rate of the reaction.

67. The second step, which is slow, is: $\text{H}_2 + \text{N}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$. The rate of this rate-determining step is: $\text{Rate} = k_2 [\text{H}_2][\text{N}_2\text{O}_2]$. Substituting for $[\text{N}_2\text{O}_2]$ gives

Rate = $\frac{k_2 k_1}{k_{-1}} [\text{H}_2] [\text{NO}]^2$. The reaction is first-order in $[\text{H}_2]$ and second-order in $[\text{NO}]$. This result conforms to the experimentally determined reaction order.



71. $\frac{d(\text{S}_1 : \text{S}_2)}{dt} = k_2 (\text{S}_1 : \text{S}_2)^* = \frac{k_2 \cdot k_1 [\text{S}_1] [\text{S}_2]}{k_{-1} + k_2}$

Integrative and Advanced Exercises

74a. First-order

74b. 0.29 min^{-1}

74c. 0.103 M/min

74d. 0.064 M/min

74e. 0.29_4 M/min.

75. 1.86 M

78. $\{\text{Units of } k\} = \text{M}_{1-0} \text{ s}^{-1}$

82. $1.9 \times 10^2 \text{ min}$

87. $\text{rate}_{\text{overall}} = k_2 [\text{CHCl}_3] \left(\frac{k_1}{k_{-1}} [\text{Cl}_2(\text{g})] \right)^{1/2}, \quad k = 0.015.$

90. $1.067 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$

91. 0.0275 s^{-1}

94a. First step.

94b. No

94c. Yes

95a. Both reactions are first-order.

95b. The second step.

95c. 0.9235 M

95d. 0.731 M N₂O

Feature Problems

96a.

Time, min	0	3	6	9	12	15	18	21	24	27	30	∞
V _{N₂} , mL	0	10.8	19.3	26.3	32.4	37.3	41.3	44.3	46.5	48.4	50.4	58.3
[C ₆ H ₅ N ₂ Cl], mM	71	58	47	39	32	26	21	17	14	12	10	0

time(min)	0	3	6	9	12	15	18	21	24	27	30	∞
ΔT(min)		3	3	3	3	3	3	3	3	3	3	
[C ₆ H ₅ N ₂ Cl](mM)	71	58	47	39	32	26	21	17	14	12	10	∞
Δ[C ₆ H ₅ N ₂ Cl](mM)		-13	-11	-8	-7	-6	-5	-4	-3	-2	-2	
96b. Reaction Rate (mM min ⁻¹)		4.3	3.7	2.7	2.3	2.0	1.7	1.3	1.0	0.7	0.7	

96c.

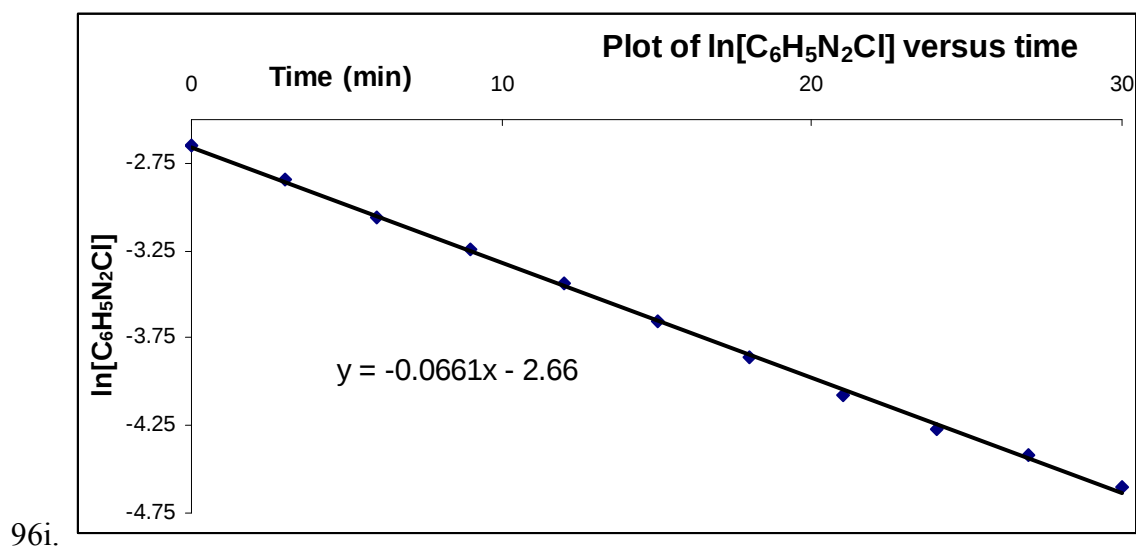
96d. 1.1×10^{-3} M min⁻¹

96e. 5.5×10^{-3} M min⁻¹

96f. Rate = k [C₆H₅N₂Cl], $k_{\text{avg}} = 0.071$ min⁻¹.

96g. Calculated half-life = 9.8 min, estimated half-life = 10.5 min.

96h. About 20 minutes.



96j. 0.0661 min^{-1}

97a. First-order in $\text{S}_2\text{O}_8^{2-}$, first-order in I^- , second-order overall.

97b. $3.7 \times 10^{-5} \text{ M s}^{-1}$

97c. $6.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$

97d. $0.0014 \text{ M}^{-1} \text{ s}^{-1}$, $0.0030 \text{ M}^{-1} \text{ s}^{-1}$, $0.0062 \text{ M}^{-1} \text{ s}^{-1}$, $0.012 \text{ M}^{-1} \text{ s}^{-1}$.

97e. 51 kJ/mol

97f. The mechanism is consistent with the stoichiometry. The rate of the slow step of the mechanism is $\text{Rate}_1 = k_1 [\text{S}_2\text{O}_8^{2-}]^1 [\text{I}^-]^1$. This is exactly the same as the experimental rate law. It is reasonable that the first step be slow since it involves two negatively charged species coming together. We know that like charges repel, and thus this should not be an easy or rapid process.

Self-Assessment Exercises

101. The answer is (c).

102. The answers are (b) and (e).

103. The answer is (a).

104. The answer is (d).

105. The answer is (b).

106. The answer is (c).

107. $3.0 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}$

108a. 60.0 min

108b. 45.0 min

109. The reaction is second-order, because the half-life doubles with each successive half-life period.

110a. 0.024 M/min

110b. 2.312 M

110c. 1.33 M

111a. $\frac{d[\text{C}]}{dt} = k_1 [\text{A}][\text{B}]$. This agrees with the observed reaction rate law.

111b. Adding the two reactions given, we still get the same overall stoichiometry as part (a). However, with the given proposed reaction mechanisms, the rate law for the product(s) is given

as follows: $\frac{d[C]}{dt} = \frac{k_2 k_1 [A][B]^2}{k_{-1} + k_2 [A]}$. This does not agree with the observed reaction rate law.

112. The answer is (b).

113. The answer is (a).

114. The answer is (d).

115. The answer is (c)

Chapter 15 Answers

Practice Examples

1a. $[\text{Cu}^{2+}] = \frac{x}{1.22}$

1b. $\approx 0.0098 \text{ M}$

2a. 8.3×10^2

2b. 6.9×10^{-5}

3a. 1.7×10^{-6}

3b. 95

4a. $K_c = \frac{[\text{Ca}^{2+}]^5 [\text{HPO}_4^{2-}]^3}{[\text{H}^+]^4}$

4b. $K_p = \frac{\{P(\text{H}_2)\}^4}{\{P(\text{H}_2\text{O})\}^4}$, $K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$, $K_p = K_c$.

5a. There will be greater quantities of reactants, and smaller quantities of products than there were initially.

5b. The net reaction will proceed to the right.

6a. The equilibrium system will shift right.

6b. (a) Adding extra CaO(s) will have no direct effect on the position of equilibrium; (b) The reaction will shift left; (c) Addition of solid CaCO_3 will not have an effect upon the position of equilibrium.

7a. Decreasing the cylinder volume would have the initial effect of doubling both $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$. In order to reestablish equilibrium, some NO_2 will then be converted into N_2O_4 . Note, however, that the NO_2 concentration will still ultimately end up being higher than it was prior to pressurization.

7b. A change in overall volume or total gas pressure will have no effect on the position of equilibrium.

8a. Greater

8b. Greater

9a. 2.3×10^{-4}

9b. 25.2 g N₂O₄

10a. $K_c = 1.5 \times 10^{-4}$, $K_p = 3.7 \times 10^{-3}$.

10b. $K_p \approx 0.022$

11a. 0.481 atm

11b. 0.716 atm

12a. 0.262 mol HI

12b. (a) The amount of N₂O₄ will decrease; (b) 0.0118 mol.

13a. $[Ag^+] = [Fe^{2+}] = 0.488 \text{ M}$, $[Fe^{3+}] = 1.20 - 0.488 = 0.71 \text{ M}$.

13b. $[V^{3+}] = [Cr^{2+}] = 0.0057 \text{ M}$, $[V^{2+}] = [Cr^{3+}] = 0.154 \text{ M}$.

Integrative Example

A. $[F6P]_{eq} = 1.113 \times 10^{-6}$. F6P will decrease with an increase in temperature.

B. (a) 8.47 L; (b) ~8.47 L.

Exercises

1a. $2 \text{ COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$, $K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$

1b. $\text{Cu}(\text{s}) + 2 \text{ Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2 \text{ Ag}(\text{s})$, $K_c = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$

1c. $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{ Fe}^{2+}(\text{aq}) \rightleftharpoons 2 \text{ SO}_4^{2-}(\text{aq}) + 2 \text{ Fe}^{3+}(\text{aq})$, $K_c = \frac{[\text{SO}_4^{2-}]^2 [\text{Fe}^{3+}]^2}{[\text{S}_2\text{O}_8^{2-}] [\text{Fe}^{2+}]^2}$

3a. $K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$

3b. $K_c = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$

$$3c. K_c = \frac{[\text{OH}^-]^2}{[\text{CO}_3^{2-}]}$$

$$5a. K_c = \frac{[\text{HF}]}{[\text{H}_2]^{1/2} [\text{F}_2]^{1/2}}$$

$$5b. K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$5c. K_c = \frac{[\text{N}_2\text{O}]^2}{[\text{N}_2]^2[\text{O}_2]}$$

$$5d. K_c = \frac{1}{[\text{Cl}_2]^{1/2} [\text{F}_2]^{3/2}}$$

$$7a. 0.0012$$

$$7b. 5.55 \times 10^5$$

$$7c. 0.429$$

$$9. K_p = 0.0313, K_c = 1.28 \times 10^{-3}.$$

$$11. 9.7 \times 10^{-16}$$

$$13. 5 \times 10^{14}$$

$$15. K = a(\text{H}_2\text{CO}_3)/a(\text{CO}_2), K = \frac{[\text{H}_2\text{CO}_3]/c^\circ}{P_{\text{CO}_2}/P^\circ}.$$

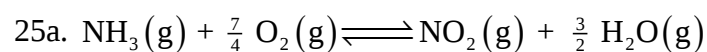
$$17. 0.106$$

$$19a. 26.3$$

$$19b. 0.613$$

$$21. 9.1 \times 10^{-18} \text{ M}$$

$$23. 0.516$$



$$25b. 4.03 \times 10^{19}$$

$$27a. K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{\frac{n\{\text{CO}\}}{V} \times \frac{n\{\text{H}_2\text{O}\}}{V}}{\frac{n\{\text{CO}_2\}}{V} \times \frac{n\{\text{H}_2\}}{V}}. \text{ Since } V \text{ is present in both the denominator and the}$$

numerator, it can be stricken from the expression.

$$27b. K_c = K_p = 0.659.$$

29. $Q_c = 0.82 < K_c = 100$. The mixture described cannot be maintained indefinitely.

31a. The mixture is not at equilibrium.

31b. The reaction will proceed to the right.

33. Amount H_2 = amount I_2 = 0.033 mol. Amount HI = 0.234 mol HI .

$$35. 4.0 \times 10^{-4} \text{ mol Cl}_2$$

$$37a. n_{\text{PCl}_5} = 0.478 \text{ mol PCl}_5, n_{\text{PCl}_3} = 0.623 \text{ mol PCl}_3, n_{\text{Cl}_2} = x = 0.0725 \text{ mol Cl}_2.$$

$$37b. \text{Amount PCl}_3 = 0.20 \text{ mol} = \text{amount Cl}_2. \text{Amount PCl}_5 = 0.41 \text{ mol}.$$

39a. The reaction will shift to the left.

39b. 26 g $\text{C}_2\text{H}_5\text{OH}$, 35 g $\text{CH}_3\text{CO}_2\text{H}$, 32 g $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$, 68 g H_2O .

41. 5.58 atm

45. Sketch (b) is the best representation because it contains numbers of SO_2Cl_2 , SO_2 , and Cl_2 molecules that are consistent with the K_c for the reaction.

$$47. K = \frac{[\text{aconitate}]}{[\text{citrate}]}, Q = \frac{4.0 \times 10^{-5}}{(0.00128)} = 0.031. \text{ Since } Q = K, \text{ the reaction is at equilibrium.}$$

49. 749.0 mmHg

51. 0.529 atm O_2 , $P_{\text{total}} = 0.601 \text{ atm total}$.

53a. 30.14 atm

53b. 32.46 atm

55. Continuous removal of the product has the effect of decreasing the concentration of the products below their equilibrium values. Thus, the equilibrium system is disturbed by removing the products and the system will attempt to re-establish the equilibrium by shifting toward the right, that is, to generate more products.

57a. Decreases

57b. Increases

57c. No change

57d. No change

59a. More NO(g) formed.

59b. Rate increases.

61. $P\{N_2(g)\}$ will have decreased when equilibrium is re-established.

63a. Shifts right, toward products .

63b. No shift, no change in equilibrium position.

63c. Shifts right, towards products .

65a. Hb:O₂ is reduced.

65b. No effect.

65c. Hb:O₂ increases.

67. The pressure on N₂O₄ will initially increase as the crystal melts and then vaporizes, but over time the new concentration decreases as the equilibrium is shifted toward NO₂.

69. While the amount of calcium carbonate will decrease, its concentration will remain the same because it is a solid.

Integrative and Advanced Exercises

73. $[Fe^{2+}] = 0.111\text{ M}$, $[Ag^+] = 0.15\text{ M}$, $[Fe^{3+}] = 0.049\text{ M}$.

74. 2.79 atm

76. 2.1×10^{-3}

78. 12.0

81. 0.177

82. 87.1 g/mol

85. 3.34×10^{-4}

87. 0.085 moles CH₄(g) , 0.070 moles H₂O(g) , 0.12 mol CO₂ , 0.16 mol H₂.

91. 24.6 atm

Feature Problems

92. 4.0

94. 4.80×10^{-8}

97. $C(\text{or}) = 6 \times 10^{-4} \text{ M}$, $C(\text{aq}) = 4 \times 10^{-4} \text{ M}$.

Self-Assessment Exercises

101. The answer is (c).

102. The answer is (d).

103. The answer is (a).

104. The answer is (b).

105. The answer is (a).

106. The answer is (c).

107. 1.9

108a. More Cl_2 is produced.

108b. Less Cl_2 is made.

108c. Less Cl_2 is made.

108d. No change.

108e. Less Cl_2 is made.

109. $\text{SO}_2 (\text{g})$ will be less than $\text{SO}_2 (\text{aq})$.

110. There will be much more product than reactant.

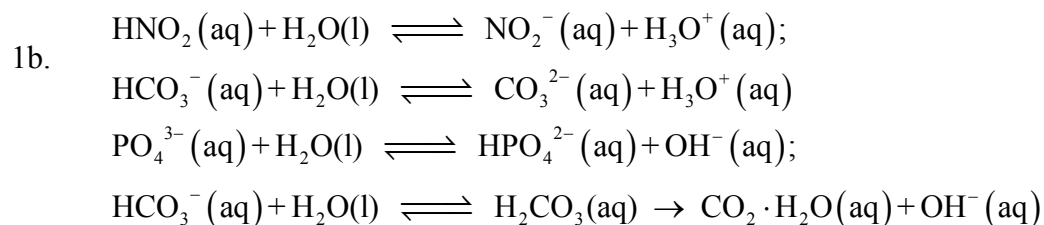
111a. 0.0578 moles

111b. 0.232 moles

Chapter 16 Answers

Practice Examples

1a. (a) Forward direction: HF is the acid and H₂O is the base. Reverse direction: F⁻ is the base and H₃O⁺ is the acid. (b) Forward direction: HSO₄ is the acid and NH₃ is the base. Reverse direction: SO₄²⁻ is the base and NH₄⁺ is the acid. (c) Forward direction: HCl is the acid and C₂H₃O₂⁻ is the base. Reverse direction: Cl⁻ is the base and HC₂H₃O₂ is the acid.



2a. $[\text{H}_3\text{O}^+] = 1.4 \times 10^{-3}$, $[\text{OH}^-] = 7.1 \times 10^{-12}$ M.

2b. 3.1 L

3a. $[\text{I}^-] = [\text{H}_3\text{O}^+] = 0.0025$ M. $[\text{OH}^-] = 4.0 \times 10^{-12}$ M.

3b. 1.670

4a. 11.519

4b. 13.739

5a. 2.9×10^{-8}

5b. 2.6×10^{-6}

6a. 1.8

6b. 2.66

7a. 2.29

7b. 11.28

8a. 17%

8b. 1.4×10^{-4}

9a. $[\text{H}_3\text{O}^+] = [\text{HOOCCH}_2\text{COO}^-] = 3.7 \times 10^{-2}$ M. $[\text{OOCCH}_2\text{COO}^-] = 2.0 \times 10^{-6}$ M.

9b. $K_{a_1} = 5.3 \times 10^{-2}$, $K_{a_2} = 5.3 \times 10^{-5}$.

10a. $[\text{SO}_4^{2-}] = 0.010\text{M}$, $[\text{H}_3\text{O}^+] = 0.21\text{ M}$, $[\text{HSO}_4^-] = 0.19\text{ M}$.

10b. $[\text{HSO}_4^-] = 0.014\text{ M}$, $[\text{H}_3\text{O}^+] = 0.026\text{ M}$, $[\text{SO}_4^{2-}] = 0.0060\text{M}$.

11a. (a) acidic; (b) neutral; (c) basic.

11b. $\text{H}_2\text{PO}_4^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{HPO}_4^{2-} (\text{aq}) \quad K_{a_2} = 6.3 \times 10^{-8}$

$\text{H}_2\text{PO}_4^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^- (\text{aq}) + \text{H}_3\text{PO}_4 (\text{aq}) \quad K_b = 1.4 \times 10^{-12}$

12a. Codeine hydrochloride

12b. Basic

13a. 8.08

13b. $3.6 \times 10^{-3}\text{M}$

14a. HClO_4 and CH_2FCOOH are the stronger acids in the pairs.

14b. H_2SO_3 and $\text{CCl}_2\text{FCH}_2\text{COOH}$ are the stronger acids in the pairs.

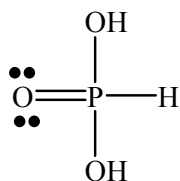
15a. (a) BF_3 is a Lewis acid and NH_3 is a Lewis base. (b) H_2O is a Lewis base and Cr^{3+} is a Lewis acid.

15b. Hydroxide ion and the chloride ion are the Lewis bases. $\text{Al}(\text{OH})_3$ and SnCl_4 are the Lewis acids.

Integrative Example

A. $\text{pH} = 5.68 \approx 5.7$

B. (a) Determine values of m and n in the formula $\text{EO}_m(\text{OH})_n$. HOCl or $\text{Cl}(\text{OH})$ has $m = 0$ and $n = 1$. We expect $K_a \approx 10^{-7}$ or $\text{p}K_a \approx 7$, which is in good agreement with the accepted $\text{p}K_a = 7.52$. HOClO or $\text{ClO}(\text{OH})$ has $m = 1$ and $n = 1$. We expect $K_a \approx 10^{-2}$ or $\text{p}K_a \approx 2$, in good agreement with the $\text{p}K_a = 1.92$. HOClO_2 or $\text{ClO}_2(\text{OH})$ has $m = 2$ and $n = 1$. We expect K_a to be large and in good agreement with the accepted value of $\text{p}K_a = -3$, $K_a = 10^{-\text{p}K_a} = 10^3$. HOClO_3 or $\text{ClO}_3(\text{OH})$ has $m = 3$ and $n = 1$. We expect K_a to be very large and in good agreement with the accepted $K_a = -8$, $\text{p}K_a = -8$, $K_a = 10^{-\text{p}K_a} = 10^8$ which turns out to be the case. (b) $K_a = 10^{-2}$. (c)



Exercises

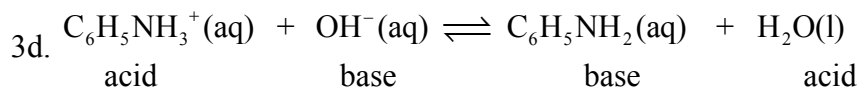
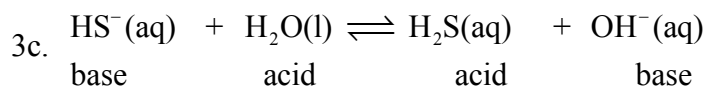
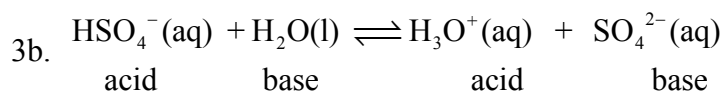
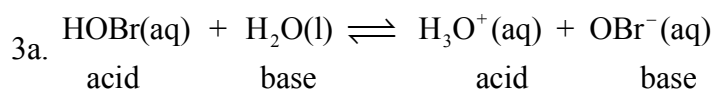
1a. Acid

1b. Base

1c. Base

1d. Acid

1e. Acid



5. Answer (b).

7a. Forward

7b. Reverse

7c. Reverse

9a. $[\text{H}_3\text{O}^+] = 0.00165 \text{ M}$, $[\text{OH}^-] = 6.1 \times 10^{-12} \text{ M}$.

9b. $[\text{OH}^-] = 0.0087 \text{ M}$, $[\text{H}_3\text{O}^+] = 1.1 \times 10^{-12} \text{ M}$.

9c. $[\text{OH}^-] = 0.00426 \text{ M}$, $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-12} \text{ M}$.

9d. $[\text{H}_3\text{O}^+] = 5.8 \times 10^{-4} \text{ M}$, $[\text{OH}^-] = 1.7 \times 10^{-11} \text{ M}$.

11. $[\text{H}_3\text{O}^+] = 4.0 \times 10^{-14} \text{ M}$, $\text{pH} = 13.40$.

13. $1.96 \times 10^{-3} \text{ M}$

15. 8.5 mL

17. 53.9 mL acid

19. 10.20

21. $[\text{H}_3\text{O}^+] = 0.0098 \text{ M}$, $\text{pH} = 2.01$.

23a. 0.0030 M

23b. 2.62

25. 2.7×10^{-3}

27. 1.4 g $\text{HC}_7\text{H}_5\text{O}_2$

29. $[\text{H}_3\text{O}^+] = 0.073 \text{ M}$, $\text{pH} = 1.14$, $\text{pOH} = 12.86$, $[\text{OH}^-] = 1.4 \times 10^{-13} \text{ M}$.

31. 11.04

33. 0.063 g vinegar

35a. 11.23

35b. 34 mg of NaOH

37. Sketch (b)

39a. 0.0053

39b. 0.53%

41. 0.0098 M

43. We would not expect these ionizations to be correct because the calculated degree of ionization is based on the assumption that the $[\text{HC}_2\text{H}_3\text{O}_2]_{\text{initial}} \approx [\text{HC}_2\text{H}_3\text{O}_2]_{\text{initial}} - [\text{HC}_2\text{H}_3\text{O}_2]_{\text{equil.}}$, which is invalid at the 13 and 42 percent levels of ionization seen here.

45. Because H_3PO_4 is a weak acid, there is little HPO_4^{2-} (produced in the 2nd ionization) compared to the H_3O^+ (produced in the 1st ionization). In turn, there is little PO_4^{3-} (produced in the 3rd ionization) compared to the HPO_4^{2-} , and very little compared to the H_3O^+ .

47a. $[\text{H}_3\text{O}^+] = 8.7 \times 10^{-5} \text{ M}$, $[\text{HS}^-] = 8.7 \times 10^{-5} \text{ M}$, $[\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$.

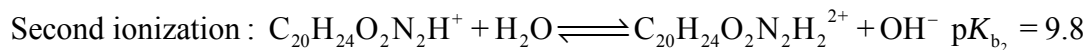
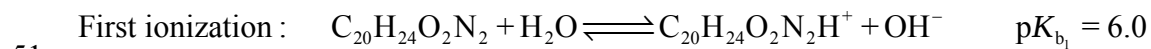
47b. $[\text{H}_3\text{O}^+] = 2.2 \times 10^{-5} \text{ M}$, $[\text{HS}^-] = 2.2 \times 10^{-5} \text{ M}$, $[\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$.

47c. $[\text{H}_3\text{O}^+] = 9.5 \times 10^{-7} \text{ M}$, $[\text{HS}^-] = 9.5 \times 10^{-7} \text{ M}$, $[\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$.

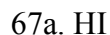
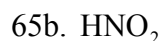
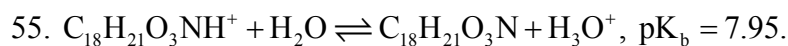
49a. $[\text{SO}_4^{2-}] = 0.011 \text{ M}$, $[\text{HSO}_4^-] = 0.74 \text{ M}$, $[\text{H}_3\text{O}^+] = 0.76 \text{ M}$.

49b. $[\text{SO}_4^{2-}] = 0.0087 \text{ M}$, $[\text{HSO}_4^-] = 0.066 \text{ M}$, $[\text{H}_3\text{O}^+] = 0.084 \text{ M}$.

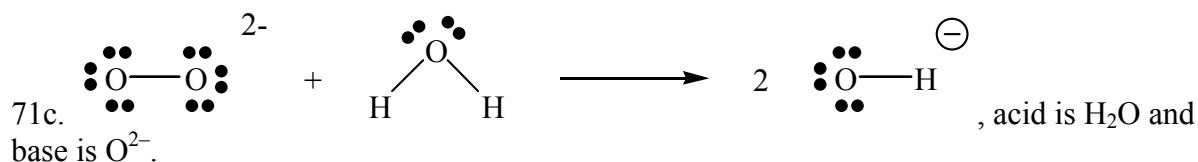
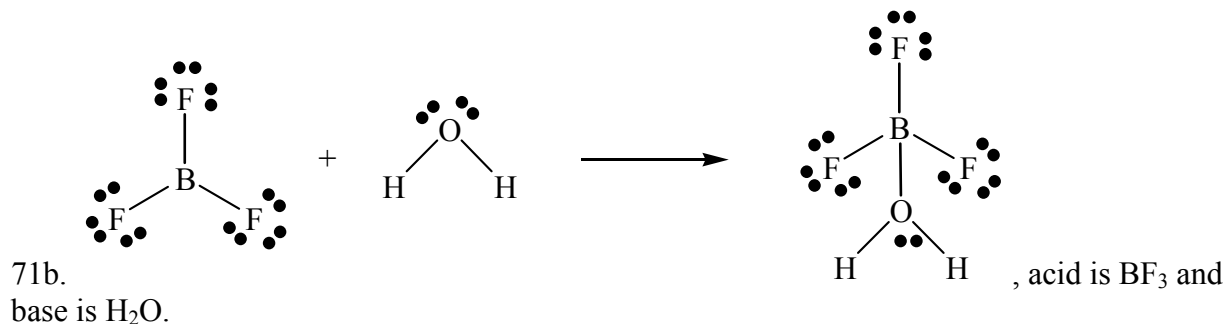
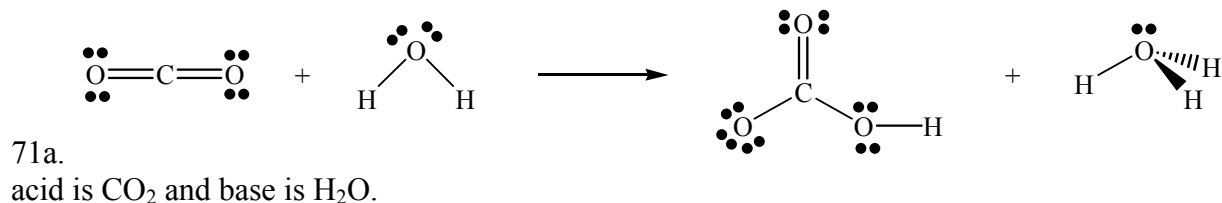
49c. $[\text{SO}_4^{2-}] = 6.6 \times 10^{-4} \text{ M}$, $[\text{HSO}_4^-] = 9 \times 10^{-5} \text{ M}$, $[\text{H}_3\text{O}^+] = 1.41 \times 10^{-3} \text{ M}$.

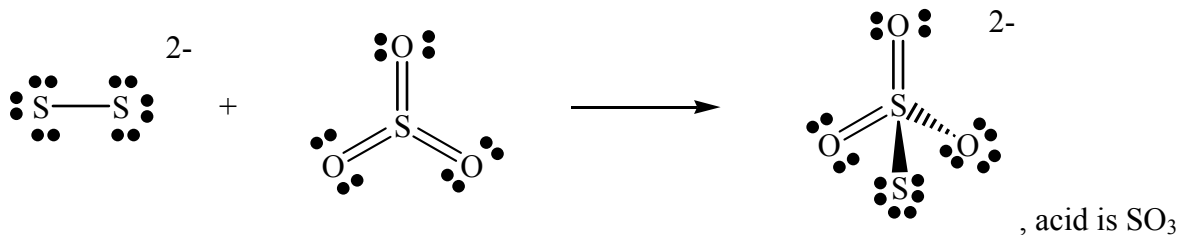


53. 9.6



69. The largest K_{b} belongs to (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$. The smallest K_{b} is that of (a) o-chloroaniline.

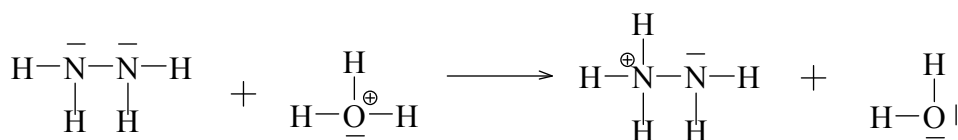
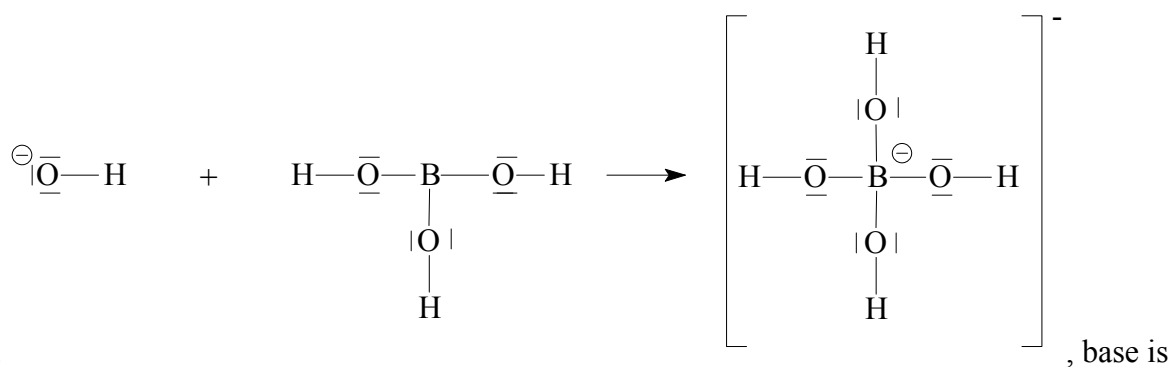




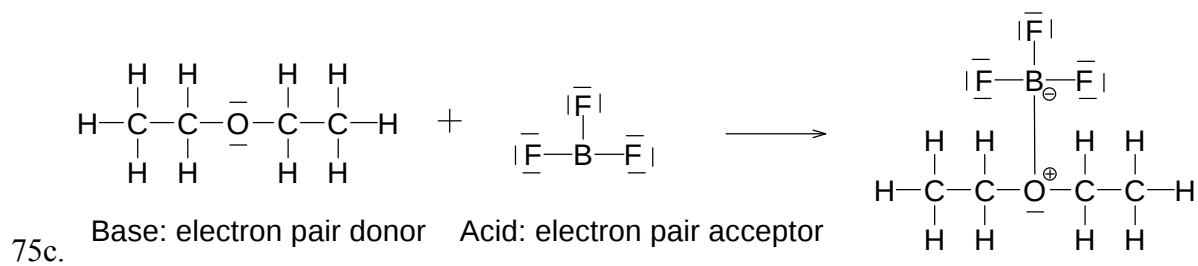
73a. Lewis base

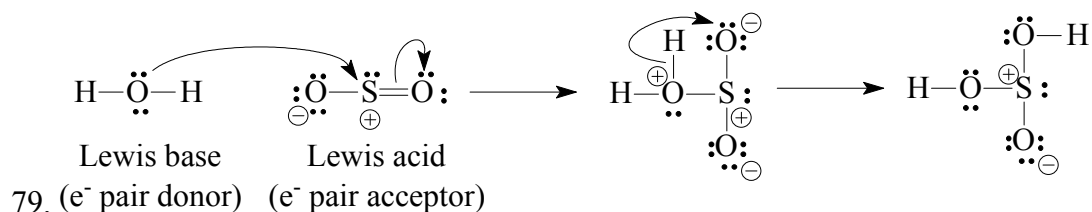
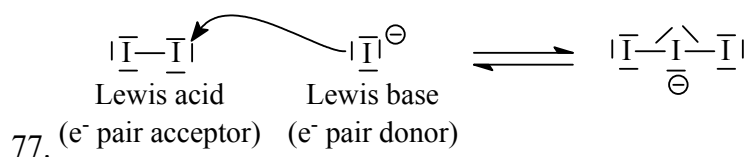
73b. Lewis acid

73c. Lewis acid



75b. The actual Lewis acid is H^+ , which is supplied by H_3O^+





Integrative and Advanced Exercises

81a. Base

81b. Base

81c. Acid or Base

81d. Acid

82. $2.10 \times 10^{-3} \text{ M}$

83a. Not matched.

83b. pH 4.6 matched.

83c. Not matched.

83d. Not matched.

83e. pH 10.8 matched.

83f. Not matched.

83g. Not matched.

83h. pH 2.1 matched.

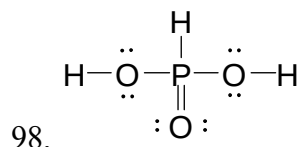
83i. Not matched.

87. 5×10^{-5}

88. 0.096 g NH_4Cl . Other solutes don't provide acidic solutions or lead to masses or volumes that are very difficult to measure.

94. 9.73 g $\text{HC}_2\text{H}_3\text{O}_2$

95. 0.16



99a. $\text{H}_2\text{SO}_3 > \text{HF} > \text{N}_2\text{H}_5^+ > \text{CH}_3\text{NH}_3^+ > \text{H}_2\text{O}$

99b. $\text{OH}^- > \text{CH}_3\text{NH}_2 > \text{N}_2\text{H}_4 > \text{F}^- > \text{HSO}_3^-$

99c. (i) to the right and (ii) to the left.

Feature Problems

102a. 2.15

102b. 11.98

102c. 9.23

Self-Assessment Exercises

106. The answer is (a).

107. The answer is (c).

108. The answer is (d).

109. The answer is (e).

110. The answer is (c).

111. The answer is (b).

112. 2.70

113. 37.2 mL

114. 8.58

115. $0.10 \text{ M HI} < 0.05 \text{ M H}_2\text{SO}_4 < 0.05 \text{ M HC}_2\text{H}_2\text{ClO}_2 < 0.50 \text{ M HC}_2\text{H}_3\text{O}_2 < 0.50 \text{ M NH}_4\text{Cl} < 1.0 \text{ M NaBr} < 0.05 \text{ M KC}_2\text{H}_3\text{O}_2 < 0.05 \text{ M NH}_3 < 0.06 \text{ M NaOH} < 0.05 \text{ M Ba(OH)}_2$

116. The solution is basic. $[\text{H}_3\text{O}^+] = 2.14 \times 10^{-12} \text{ M}$. $[\text{NH}_3] = 1.2 \text{ M}$.

117. The answer is (a).

118. The answer is (b).

119. The answer is (d).

120. 8.2

Chapter 17 Answers

Practice Examples

1a. $[\text{H}_3\text{O}^+] = 0.018 \text{ M}$, $[\text{HF}] = 0.482 \text{ M}$. $[\text{H}_3\text{O}^+] = 0.103 \text{ M}$, $[\text{HF}] = 0.497 \text{ M}$.

1b. 30 drops

2a. $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-4} \text{ M}$, $[\text{CHO}_2^-] = 0.150 \text{ M}$.

2b. 15 g $\text{NaC}_2\text{H}_3\text{O}_2$

3a. The hydronium ion and the acetate ion react to form acetic acid. All that is necessary to form a buffer is to have approximately equal amounts of a weak acid and its conjugate base together in solution. This will be achieved if we add an amount of HCl equal to approximately half the original amount of acetate ion.

3b. HCl dissociates essentially completely in water and serves as a source of hydronium ion. This reacts with ammonia to form ammonium ion. Because a buffer contains approximately equal amounts of a weak base (NH_3) and its conjugate acid (NH_4^+), to prepare a buffer we simply add an amount of HCl equal to approximately half the amount of $\text{NH}_3(\text{aq})$ initially present.

4a. 3.94

4b. 4.51

5a. 21 g

5b. $\text{pH} = 5.09 \approx 5.1$

6a. (a) 3.53; (b) 3.53; (c) 3.55.

6b. 1.3 mL

7a. (a) 0.824; (b) 1.238; (c) 7.00; (d) 11.785.

7b. (a) 12.21; (b) 11.79; (c) 7.00.

8a. (a) 2.02; (b) 2.70; (c) 3.18; (d) 8.08.

8b. (a) 11.15; (b) 9.74; (c) 9.26; (d) 5.20.

9a. 12.18

9b. 10.45

Integrative Examples

A. -0.283°C

B. 80 g/mol, $K_b = 1 \times 10^{-6}$.

Exercises

1a. 0.0892M

1b. 1.1×10^{-13} M

1c. 4.0×10^{-5} M

1d. 0.0892 M

3a. 1.05

3b. No change. The pH changes are not the same because there is an equilibrium system to be shifted in the first solution, whereas there is no equilibrium, just a change in total ionic strength, for the second solution.

5a. 0.035 M

5b. 4.0×10^{-4} M

5c. 3.9×10^{-5} M

7. 0.77 M

9a. 4.64

9b. 9.68

11a. Not a buffer.

11b. Not a buffer.

11c. Buffer

11d. Not a buffer.

11e. Buffer

11f. Not a buffer.

13. 8.88

15a. 4.8 g $(\text{NH}_4)_2\text{SO}_4$

15b. 0.41 g $(\text{NH}_4)_2\text{SO}_4$

17. 9.16

19. Use HCHO_2 and NaCHO_2 to prepare a buffer with $\text{pH} = 3.50$. $V_{\text{acid}} = 100. \text{ mL}$, $V_{\text{salt}} = 58 \text{ mL}$.

21a. $\text{pH} = 3.89$ to $\text{pH} = 5.89$.

21b. 0.100 mol of acid or base per liter of buffer solution.

23a. 3.48

23b. 3.52

23c. 1.23

25a. $\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log \frac{0.0720 \text{ M}}{0.128 \text{ M}} = 9.01 \approx 9.00$

25b. The Henderson-Hasselbalch equation depends on the assumption that:

$[\text{NH}_3] \gg 1.8 \times 10^{-5} \text{ M} \ll [\text{NH}_4^+]$. If the solution is diluted to 1.00 L, $[\text{NH}_3] = 7.20 \times 10^{-3} \text{ M}$, and $[\text{NH}_4^+] = 1.28 \times 10^{-2} \text{ M}$. These concentrations are consistent with the assumption. However, if the solution is diluted to 1000. L, $[\text{NH}_3] = 7.2 \times 10^{-6} \text{ M}$, and $[\text{NH}_4^+] = 1.28 \times 10^{-5} \text{ M}$, and these two concentrations are not consistent with the assumption. Thus, in 1000. L of solution, the given quantities of NH_3 and NH_4^+ will not produce a solution with $\text{pH} = 9.00$. With sufficient dilution, the solution will become indistinguishable from pure water (i.e.; its pH will equal 7.00).

25c. 8.99

25d. 1.1 mL 1.00 M HCl

27a. Bromphenol blue changes color in acidic solution. Bromocresol green changes color in acidic solution. Bromthymol changes color in neutral solution. 2,4-Dinitrophenol changes color in acidic solution. Chlorophenol red changes color in acidic solution. Thymolphthalein changes color in basic solution.

27b. If bromocresol green is green, the pH is probably about $\text{pH} = 4.7$. If chlorophenol red is orange, the pH is probably about $\text{pH} = 6.0$.

29a. In an Acid–Base titration, the pH of the solution changes sharply at a definite pH that is known prior to titration. Determining the pH of a solution is more difficult because the pH of the solution is not known precisely in advance. Since each indicator only serves to fix the pH over a quite small region, often less than 2.0 pH units, several indicators—carefully chosen to span the entire range of 14 pH units—must be employed to narrow the pH to ± 1 pH unit or possibly lower.

29b. An indicator is, after all, a weak acid. Its addition to a solution will affect the acidity of that solution. Thus, one adds only enough indicator to show a color change and not enough to affect solution acidity.

31a. Red

31b. Yellow

31c. Yellow

31d. Yellow

31e. Red

31f. Yellow

33. The approximate $pK_{HIn} = 3.84$. This is a relatively good indicator.

35. 0.1508 M

37. 11.63

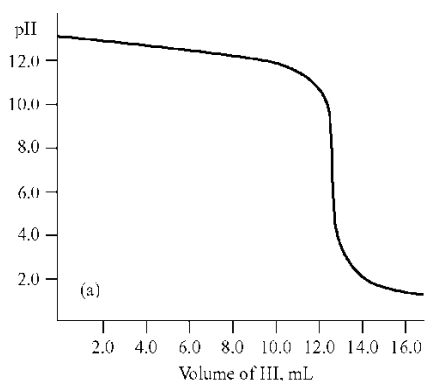
39a. 1.346

39b. 2.034

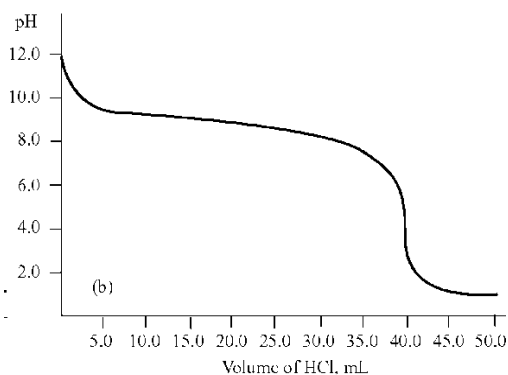
41a. 2.87

41b. 3.51

43. The volume of acid and its molarity are the same. Thus, the amount of acid is the same in each case. The volume of titrant needed to reach the equivalence point will also be the same in both cases, since the titrant has the same concentration in each case, and it is the same amount of base that reacts with a given amount (in moles) of acid. At the equivalence point in the titration of a strong acid with a strong base, the solution contains ions that do not hydrolyze. But the equivalence point solution of the titration of a weak acid with a strong base contains the anion of a weak acid, which will hydrolyze to produce a basic (alkaline) solution.



45a.

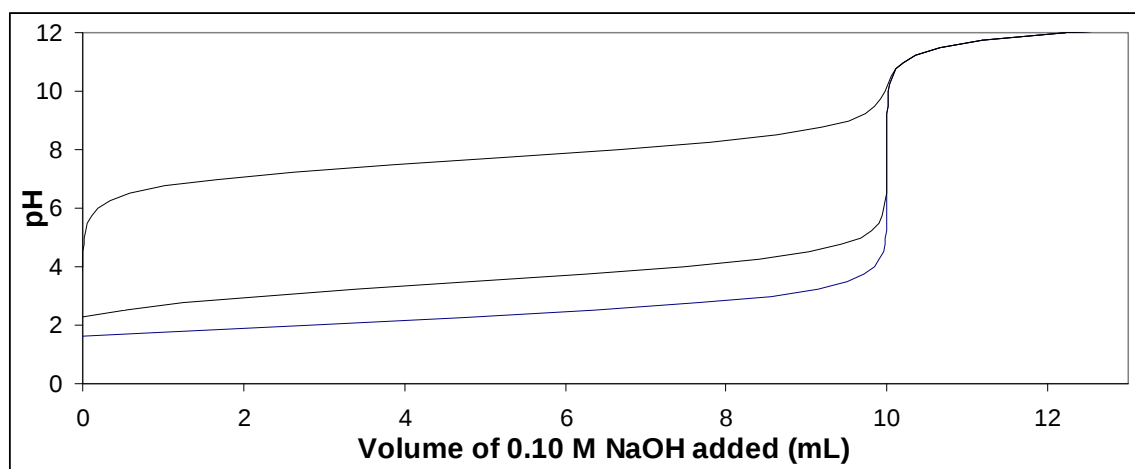


45b.

47a. 11.9 mL acid

47b. 17.4 mL acid

47c. 17.5 mL acid



49a.

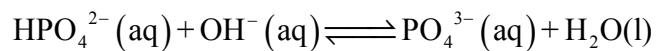
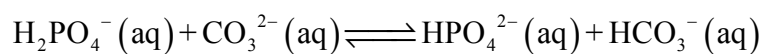
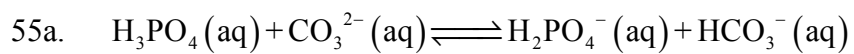
bromthymol blue

49b. See sketch in 49a. Thymol blue.

49c. See sketch in 49a. Alizarin yellow.

51.

53. Basic. This alkalinity is created by the hydrolysis of the sulfide ion, the anion of a very weak acid.



55b. CO_3^{2-} is not a strong enough base to remove the third proton from H_3PO_4 .

57. $K_{a_1} = 1.6 \times 10^{-3}$, $K_{a_2} = 1.0 \times 10^{-8}$.

59a. 0.0038 M

59b. 0.49 M

61a. No

61b. No

61c. Yes

61d. No

61e. Yes

61f. No

Integrative and Advanced Exercises

63a. $\text{HSO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

63b. 2.8%

63c. bromthymol blue or phenol red.

64a. 27.8 mL

64b. 3.3 mL

64c. 250 mL

66a. No

66b. 18%

69a. $\text{pH} = \text{pK}_a + \log(f/(1-f))$

69b. 9.56

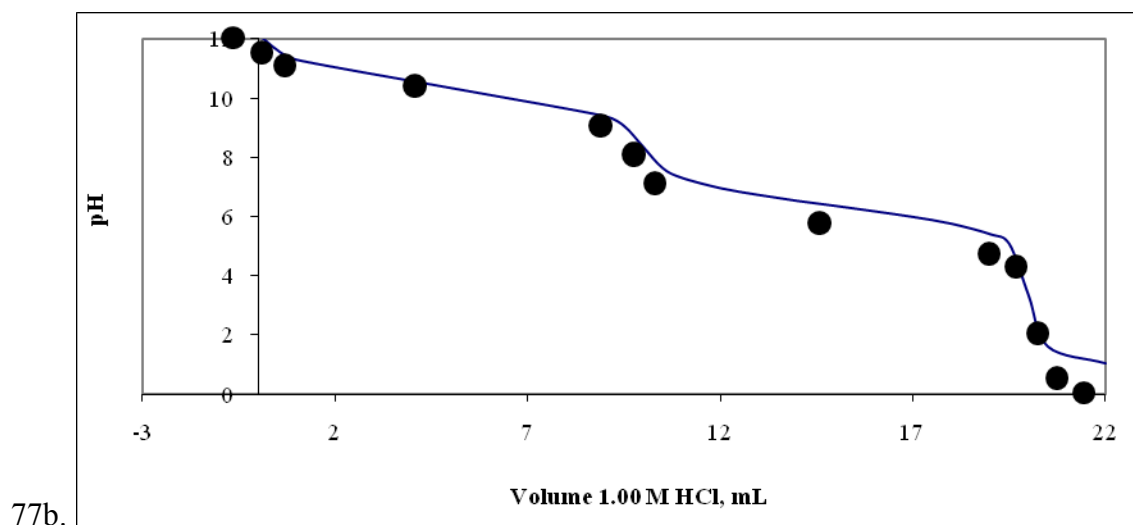
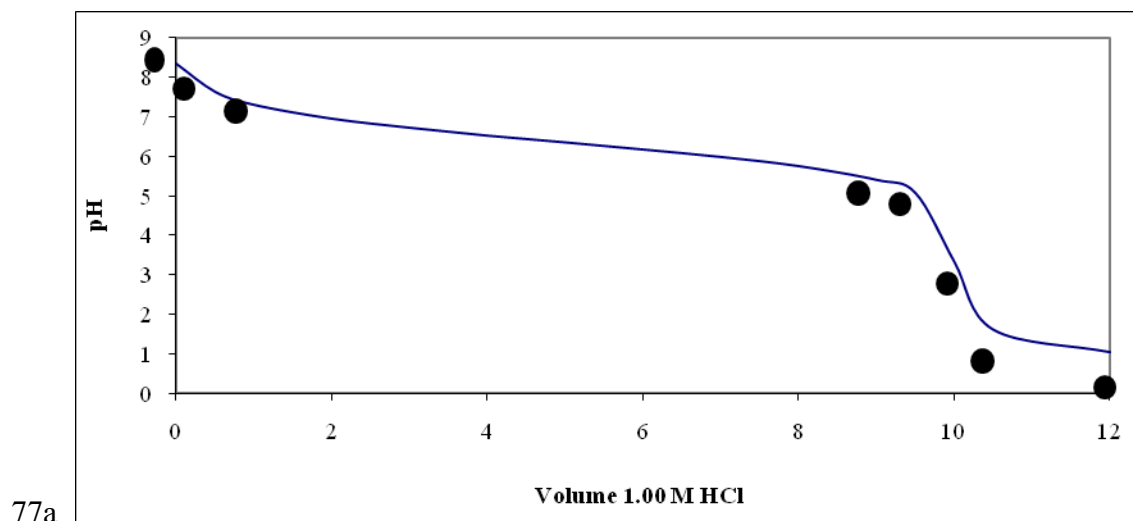
70a. 1.6

70b. 6.3 g KH_2PO_4 , 26 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

71. ~3 drops NH_3

73a. Equation (1): $K = 1.00 \times 10^{14}$. Equation (2): $K = 1.8 \times 10^9$.

73b. The extremely large size of each equilibrium constant indicates that each reaction goes essentially to completion.

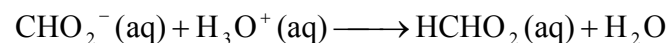


77c. 119 mL

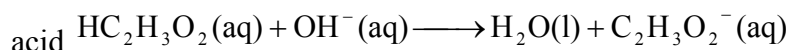
77d. 189 mL

77e. 8.3%

81a. A buffer solution is able to react with small amounts of added acid or base. When strong acid is added, it reacts with formate ion.



Added strong base reacts with acetic



Therefore neither added strong acid nor added strong base alters the pH of the solution very much. Mixtures of this type are referred to as buffer solutions.

81b. 4.40

81c. 3.8

82a. Bromthymol blue or phenol red.

82b. The $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ system.

82c. 5.4

83. 12.17

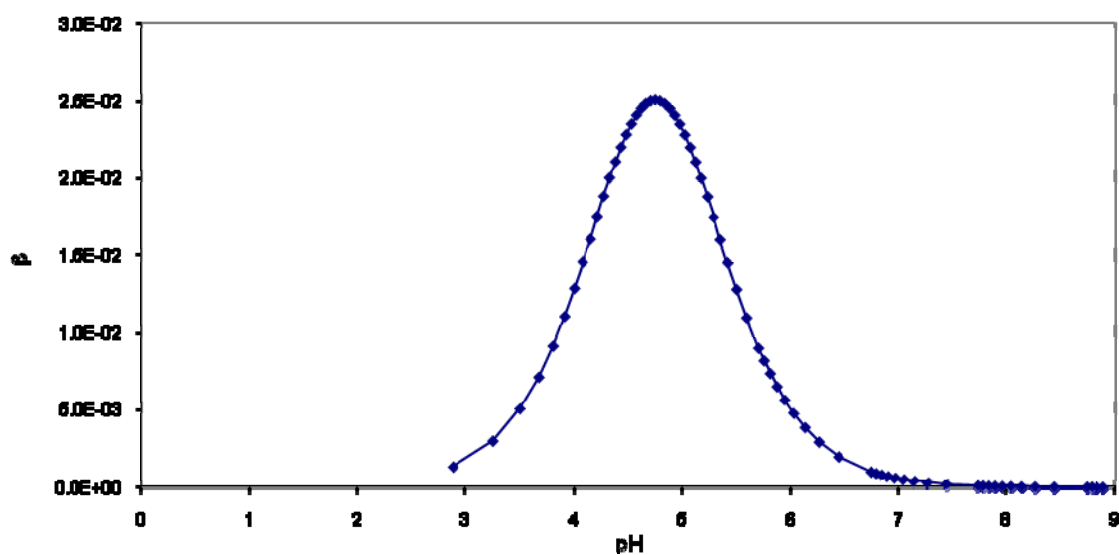
84. 8.2

$$89\text{a. } [\text{H}_3\text{O}^+] = \sqrt{\frac{K_1 [\text{CO}_2(\text{g})][\text{Ca}^{2+}]}{K_2 \cdot K_3 \cdot K_4}}$$

89b. 7.57

91a. 4.6×10^{-3}

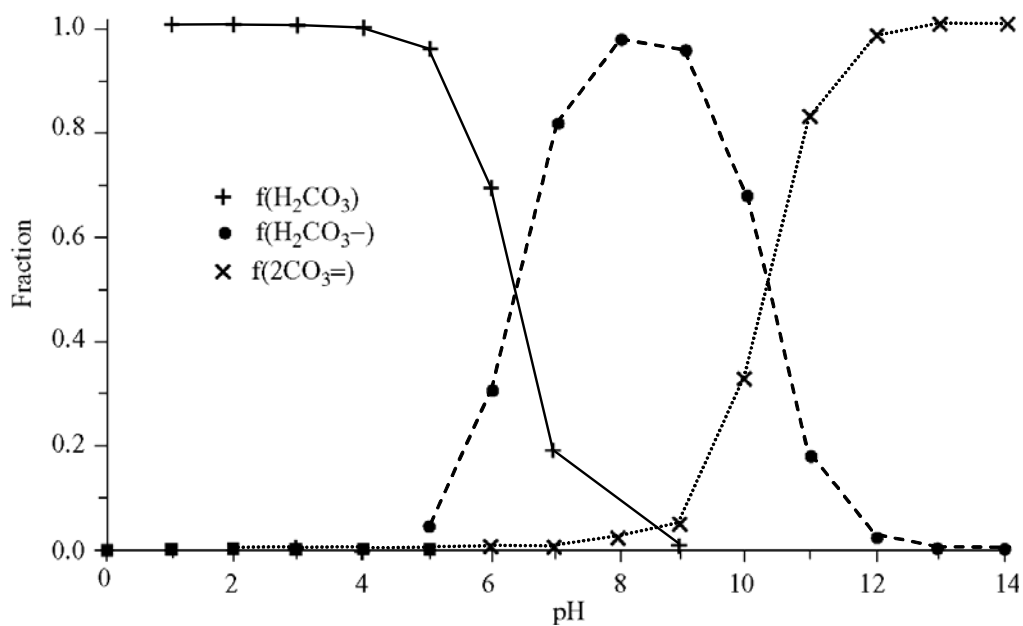
91b. 4.78



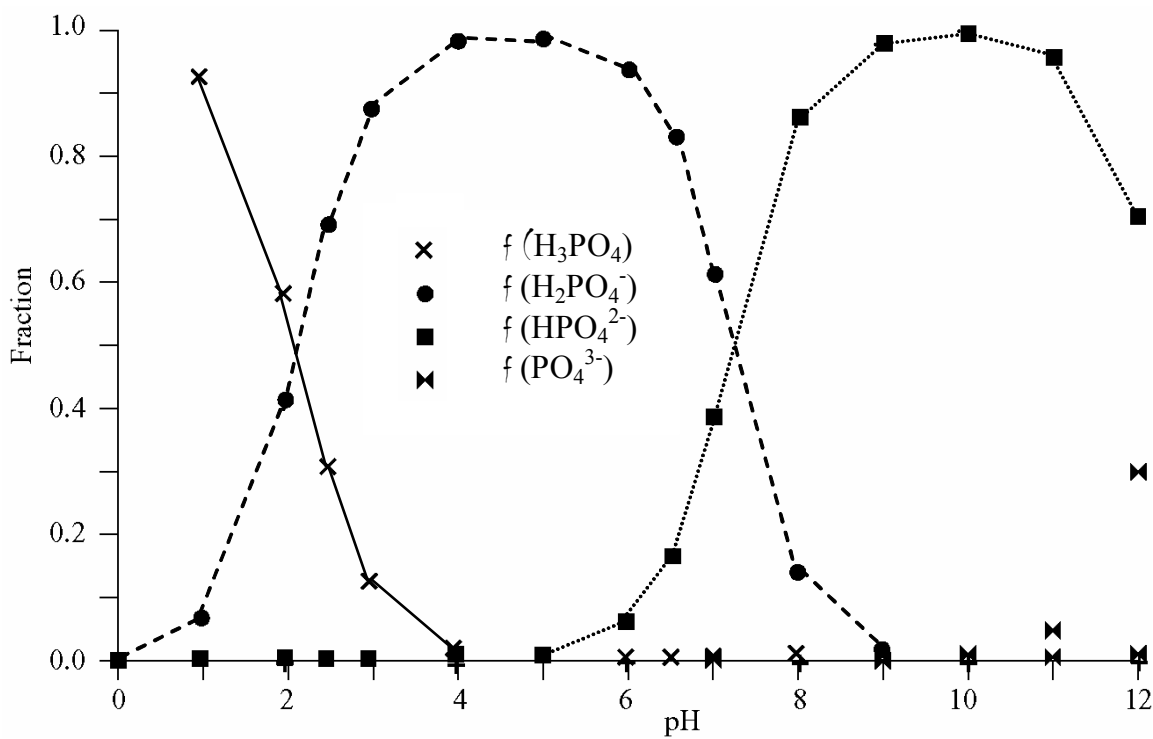
91c.

Feature Problems

92a. The two curves cross the point at which half of the total acetate is present as acetic acid and half is present as acetate ion. This is the half equivalence point in a titration, where $\text{pH} = \text{p}K_a = 4.74$.

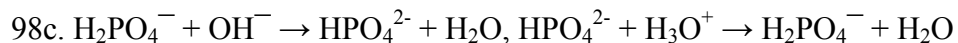
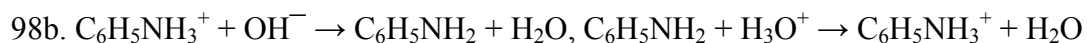


92b.

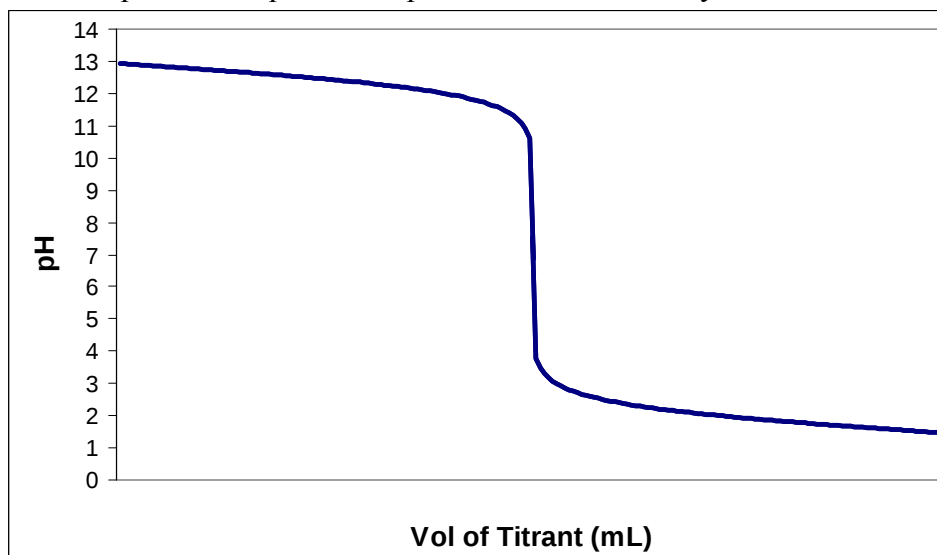


92c.

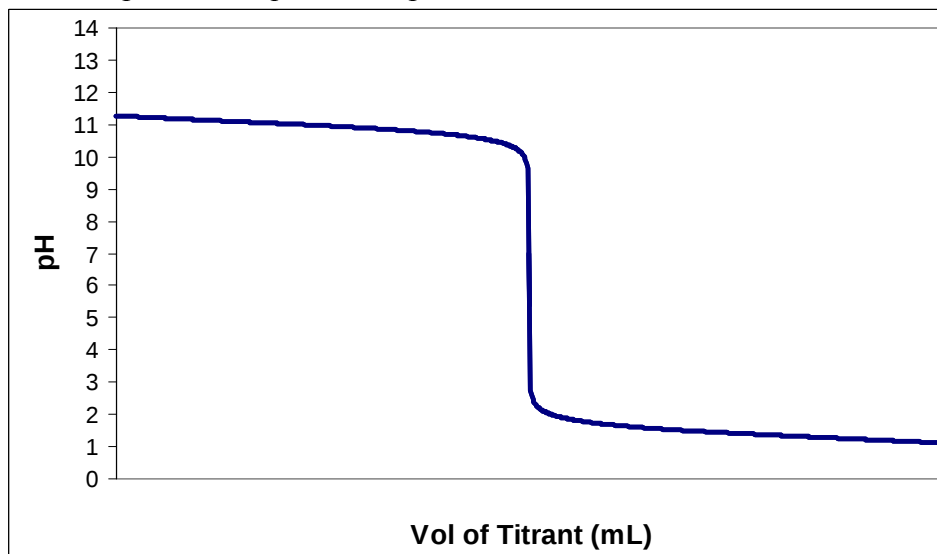
Self-Assessment Exercises



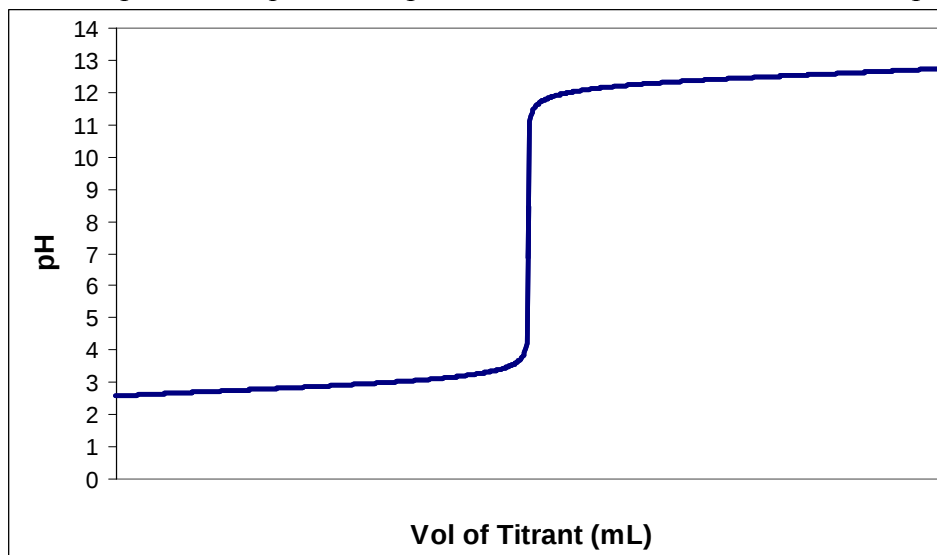
99a. The pH at the equivalence point is 7. Use bromthymol blue.



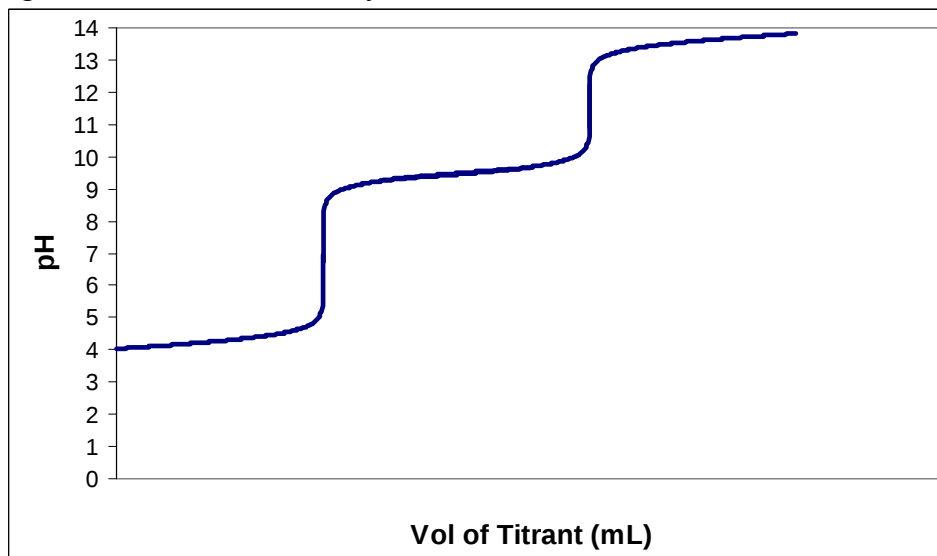
99b. The pH at the equivalence point is ~5.3 for a 0.1 M solution. Use methyl red.



99c. The pH at the equivalence point is ~8.7 for a 0.1 M solution. Use phenolphthalein.



99d. The pH for the first equivalence point ($\text{NaH}_2\text{PO}_4^-$ to $\text{Na}_2\text{HPO}_4^{2-}$) for a 0.1 M solution is right around ~7. Use bromthymol blue.



100a. 3.12

100b. 4.20

100c. 8.00

100d. 11.1

101. The answer is (c).

102. The answer is (d).

103. The answer is (b).

104. The answer is (b).

105. 10.32

106. 8.75

107. The answer is (a).

108. The answer is (b).

109. The answer is (b).

110a. $\text{pH} > 7$

110b. $\text{pH} < 7$

110c. $\text{pH} = 7$

Chapter 18 Answers

Practice Examples

1a. (a) $K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$; (b) $K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$.

1b. (a) $\text{CaHPO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$; (b) $K_{sp} = [\text{Ca}^{2+}][\text{HPO}_4^{2-}]$.

2a. 3×10^{-7}

2b. 1.9×10^{-9}

3a. $3.7 \times 10^{-8} \text{ M}$

3b. 0.55 mg

4a. $1.3 \times 10^{-4} \text{ M}$

4b. $9.8 \times 10^{-21} \text{ M}$

5a. Yes

5b. 10 drops

6a. No

6b. 0.02 M

7a. 0.12%

7b. Chromate. $[\text{Ba}^{2+}] = 5.5 \times 10^{-7} \text{ M}$.

8a. No

8b. Yes

9a. 0.074 M

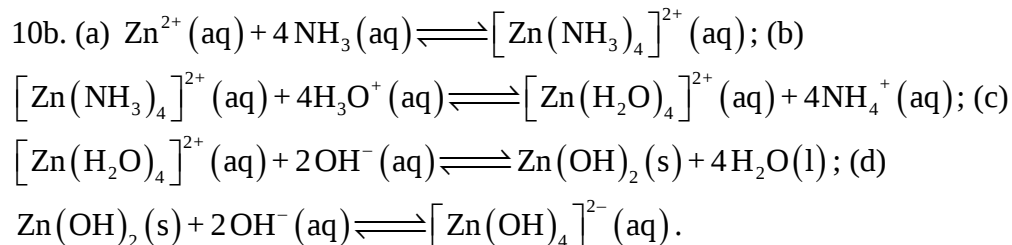
9b. $8.7 \times 10^{-3} \text{ M}$

10a. (a) $\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{s})$; (b)

$\text{Cu}(\text{OH})_2(\text{s}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$; (c)

$\text{Cu}(\text{OH})_2(\text{s}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$,

$\text{Cu}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$.



11a. Yes

11b. No

12a. 0.58 M

12b. 0.20 M

13a. $4 \times 10^{-6} \text{ M}$

13b. In Example 18-13 the expression for the solubility, s , of a silver halide in an aqueous ammonia solution, where $[\text{NH}_3]$ is the concentration of aqueous ammonia, was given by:

$$\sqrt{K_{\text{sp}} \times K_{\text{f}}} = \frac{s}{[\text{NH}_3] - 2s} . \text{ For all scenarios, the } [\text{NH}_3] \text{ stays fixed at } 0.1000 \text{ M and}$$

K_{f} is always 1.6×10^7 . We see that s will decrease as does K_{sp} .

14a. For FeS, $Q_{\text{spa}} = 0.022 < 6 \times 10^{-2} = K_{\text{spa}}$, for Ag_2S , $Q_{\text{spa}} = 1.1 \times 10^{-4} > 6 \times 10^{-30} = K_{\text{spa}}$.

14b. 2.7

Integrative Examples

A. $87 \times 10^6 \text{ g Ca}(\text{NO}_3)_2$

B. Ag_2SO_4 . No precipitate is remaining.

Exercises

1a. $K_{\text{sp}} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$

1b. $K_{\text{sp}} = [\text{Ra}^{2+}] [\text{IO}_3^-]^2$

1c. $K_{\text{sp}} = [\text{Ni}^{2+}]^3 [\text{PO}_4^{3-}]^2$

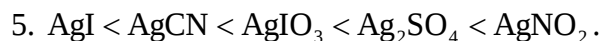
1d. $K_{\text{sp}} = [\text{PuO}_2^{2+}] [\text{CO}_3^{2-}]$

$$3a. K_{sp} = [\text{Cr}^{3+}][\text{F}^-]^3 = 6.6 \times 10^{-11}$$

$$3b. K_{sp} = [\text{Au}^{3+}]^2[\text{C}_2\text{O}_4^{2-}]^3 = 1 \times 10^{-10}$$

$$3c. K_{sp} = [\text{Cd}^{2+}]^3[\text{PO}_4^{3-}]^2 = 2.1 \times 10^{-33}$$

$$3d. K_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2 = 2.5 \times 10^{-9}$$



7. Yes

9. 11 mg

11. $4.5 \times 10^{-3} \text{ M}$

13. 5.30×10^{-5}

15a. $1.7 \times 10^{-4} \text{ M}$

15b. $7.3 \times 10^{-6} \text{ M}$

15c. $1.4 \times 10^{-8} \text{ M}$

17. The presence of KI in a solution produces a significant $[\text{I}^-]$ in the solution. Not as much AgI can dissolve in such a solution as in pure water, since the ion product, $[\text{Ag}^+][\text{I}^-]$, cannot exceed the value of K_{sp} . In similar fashion, AgNO_3 produces a significant $[\text{Ag}^+]$ in solution, again influencing the value of the ion product; not as much AgI can dissolve as in pure water.

19. 1.5×10^{-5}

21. 0.079 M

23. The solubility of Ag_2CrO_4 cannot be lowered to $5.0 \times 10^{-8} \text{ M}$ with CrO_4^{2-} as the common ion. The solubility can be lowered to $5.0 \times 10^{-8} \text{ M}$ by carefully adding $\text{Ag}^+(\text{aq})$.

25. 27 ppm

27. Yes

29. $\text{pH} > 8.32$

31a. Yes

31b. Yes

31c. No

33. CaC_2O_4 should precipitate.

35. 0.052%

37. 2.5%. $[\text{Cl}^-] = 0.16 \text{ M}$.

39a. No

39b. Yes

41a. AgI

41b. $2.7 \times 10^{-4} \text{ M}$

41c. $[\text{Ag}^+] = 3.1 \times 10^{-13} \text{ M}$.

41d. Yes

43a. AgI(s)

43b. $[\text{I}^-] = 4.7 \times 10^{-9} \text{ M}$.

43c. Yes

45. MgCO_3 (s), FeS (s), $\text{Ca}(\text{OH})_2$ (s).

47. 9.60

49a. 3.41

49b. 0.96 g

51. Lead(II) ion forms a complex ion with chloride ion. It forms no such complex ion with nitrate ion. The formation of this complex ion decreases the concentrations of free $\text{Pb}^{2+}(\text{aq})$ and free $\text{Cl}^-(\text{aq})$. Thus, PbCl_2 will dissolve in the $\text{HCl}(\text{aq})$ up until the value of the solubility product is exceeded.

53. 2.0×10^{30}

55. Precipitation of AgI(s) should occur.

57. $1.4 \times 10^{-6} \text{ g}$

59. If the $[\text{H}_3\text{O}^+]$ is maintained just a bit higher than $1.8 \times 10^{-5} \text{ M}$, FeS will precipitate and $\text{Mn}^{2+}(\text{aq})$ will remain in solution. Separation will be complete.

61a. $Q_{\text{spa}} = 1.7 \times 10^7 < 3 \times 10^7 = K_{\text{spa}}$ for MnS. Precipitation will not occur.

61b. $[\text{C}_2\text{H}_3\text{O}_2^-] = 0.21\text{M}$.

63. The most important consequence would be the absence of a valid test for the presence or absence of Pb^{2+} . In addition, if NH_3 is added first, PbCl_2 may form $\text{Pb}(\text{OH})_2$. If $\text{Pb}(\text{OH})_2$ does form, it will be present with Hg_2Cl_2 in the solid, although $\text{Pb}(\text{OH})_2$ will not darken with added NH_3 . Presence of Ag^+ may be falsely concluded.

65. (a) and (c) are the valid conclusions.

Integrative and Advanced Exercises

67. 68%

69. 38%

71. 0.012 M

74. 2 g MnS/L

77a. Yes

77b. No

77c. Yes

80. 1.2×10^{-16}

82. $1.6 \times 10^{-3} \text{ M}$

83. $6.5 \times 10^{-4} \text{ M}$

85a. $\text{Ag}_2\text{SO}_4(\text{s}) + \text{Ba}^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq}) \longrightarrow \text{BaSO}_4(\text{s}) + 2 \text{AgCl}(\text{s})$

85b. 0.875 g BaSO_4 , 1.07 g AgCl , $\text{Ag}_2\text{SO}_4(\text{s}) = 0.63 \text{ g}$, mass dissolved $\text{Ag}_2\text{SO}_4 = 0.702 \text{ g}$.

Feature Problems

87. 3.0×10^{-4}

89a. $1.7 \times 10^{-4} \text{ M}$

89b. $1.7 \times 10^{-4} \text{ M}$

89c. $2.8 \times 10^{-5} \text{ M}$

89d. 0.059 M

89e. $1.4 \times 10^{-9} \text{ M}$

Self-Assessment Exercises

- 93. The answer is (d).
- 94. The answer is (a).
- 95. The answer is (c).
- 96. The answer is (b).
- 97. The answers are (c) and (d).
- 98. The answer is (a).
- 99. The answer is (c).
- 100a. More soluble in basic solution.
- 100b. More soluble in acidic solution.
- 100c. More soluble in acidic solution.
- 100d. Solubility is independent of pH.
- 100e. Solubility is independent of pH.
- 100f. More soluble in acidic solution.
- 101. The answer is NH_3 .
- 102. Yes
- 103. The answer is (b).
- 104. The answer is (d).
- 105. The answer is (b).
- 106. It will decrease the amount of precipitate.
- 107. No precipitate will form.
- 108. CuCO_3 is soluble in $\text{NH}_3(\text{aq})$ and $\text{CuS}(\text{s})$ is not.

Chapter 19 Answers

Practice Examples

1a. (a) Decreases; (b) increases.

1b. (a) Uncertain; (b) increases.

2a. $83.0 \text{ J mol}^{-1} \text{ K}^{-1}$

2b. 402 J/mol

3a. $-99.4 \text{ J mol}^{-1} \text{ K}^{-1}$

3b. $312.4 \text{ J mol}^{-1} \text{ K}$

4a. (a) Case 2; (b) case 4.

4b. (a) High temperatures; (b) low temperatures.

5a. -1484 kJ

5b. $-70.48 \text{ kJ mol}^{-1}$

6a. (a) $K = \frac{P_{\text{SiCl}_4}}{P_{\text{Cl}_2}^2} = K_p$; (b) $K = \frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{P_{\text{Cl}_2}}$.

6b. $K = \frac{[\text{Pb}^{2+}]^3 P_{\text{NO}}^2}{[\text{NO}_3^-]^2 [\text{H}^+]^8}$

7a. Non-spontaneous

7b. NO_2 will spontaneously convert into N_2O_4 .

8a. 8.5×10^{-17}

8b. No appreciable forward reaction.

9a. 607 K

9b. (a) 1.5×10^7 ; (b) 1.7×10^5 .

10a. $\approx 970^\circ \text{C}$

10b. 5×10^9

Integrative Example

A. 1.42 kJ/mol

B. $167 \text{ JK}^{-1}\text{mol}^{-1}$

Exercises

1a. Decrease

1b. Increase

1c. Increase

3. The first law of thermodynamics states that energy is neither created nor destroyed (thus, “The energy of the universe is constant”). A consequence of the second law of thermodynamics is that entropy of the universe increases for all spontaneous processes (and therefore, “the entropy of the universe increases toward a maximum”).

5a. Increase

5b. Decrease

5c. Uncertain

5d. Decrease

7a. Negative

7b. Positive

7c. Positive

7d. Uncertain

7e. Negative

9a. $\Delta H_{\text{vap}}^{\circ} = +44.0 \text{ kJ/mol}$, $\Delta S_{\text{vap}}^{\circ} = 118.9 \text{ J mol}^{-1}\text{K}^{-1}$.

9b. Hydrogen bonding is more disrupted in water at 100°C than at 25°C , and hence, there is not as much energy needed to convert liquid to vapor (thus $\Delta H_{\text{vap}}^{\circ}$ has a smaller value at 100°C).

The reason why $\Delta S_{\text{vap}}^{\circ}$ has a larger value at 25°C than at 100°C has to do with dispersion. A vapor at 1 atm pressure (the case at both temperatures) has about the same entropy. On the other hand, liquid water is more disordered (better able to disperse energy) at higher temperatures since more of the hydrogen bonds are disrupted by thermal motion.

11. $\text{C}_6\text{H}_5\text{CH}_3$

13. 354 K

15. Answer (b) is correct.

17a. Case 2

17b. No prediction

17c. Case 3

19. The process is clearly spontaneous, and therefore $\Delta G < 0$. The gases are more dispersed when they are at a lower pressure and therefore $\Delta S > 0$. $\Delta H = 0$ because the gases are ideal and thus there are no forces of attraction or repulsion between them.

21a. An exothermic reaction may not occur spontaneously if, at the same time, the system becomes more ordered (concentrated) that is, $\Delta S^\circ < 0$. This is particularly true at a high temperature, where the $T\Delta S$ term dominates the ΔG expression.

21b. A reaction in which $\Delta S > 0$ need not be spontaneous if that process also is endothermic. This is particularly true at low temperatures, where the ΔH term dominates the ΔG expression.

23. -285 J mol^{-1}

25a. $+4.4 \text{ kJ}$

25b. The reaction does not proceed spontaneously in the forward direction.

27a. -1.6 kJ , reaches equilibrium.

27b. -474.3 kJ , goes to completion.

27c. -574.2 kJ , goes to completion.

29a. -3202 kJ

29b. -3177 kJ

31a. $-0.0545 \text{ kJ K}^{-1}$

31b. -616 kJ

31c. -600 kJ . Since the $\Delta G^\circ_{\text{rxn}}$ is negative, the reaction is spontaneous, and hence feasible (at 25°C). Because both the entropy and enthalpy changes are *negative*, this reaction will be more highly favored at low temperatures.

33a. $K = K_p = K_c (RT)^{-1}$

33b. $K = K_p = K_c$

33c. $K = K_p = K_c (RT)^2$

35. $K = 14.5$, $\Delta G^\circ = -11 \text{ kJ mol}^{-1}$.

37. 8×10^{-13}

39a. $\Delta G^\circ = -76.0 \text{ kJ/mol}$, $K = 2 \times 10^{13}$.

39b. $\Delta G^\circ = -32 \text{ kJ/mol}$, $K = 4 \times 10^5$.

39c. $\Delta G^\circ = -28.1 \text{ kJ/mol}$, $K = 8 \times 10^4$.

41. The reaction is spontaneous in the forward direction.

43. The reaction is spontaneous in the forward direction.

45. Equation (b) is incorrect. The $T\Delta S^\circ$ term should be subtracted from the ΔH° term, not added to it.

47a. 0.659

47b. 3.467 kJ/mol

47c. The reaction will proceed to the right.

49a. -23.4 kJ

49b. +68.9 kJ/mol

49c. +5.40 kJ/mol

49d. +28.7 kJ/mol

51. -204.6 kJ/mol

53a. $P\{\text{O}_2(\text{g})\} = 3.0 \times 10^{-21} \text{ atm}$

53b. High temperature, which favors the products (i.e., the side with molecular oxygen.) In addition, the molecular oxygen was removed immediately after it was formed, which causes the equilibrium to shift to the right continuously.

55a. $+215.2 \frac{\text{J}}{\text{K mol}}$

55b. $+91 \frac{\text{kJ}}{\text{mol}}$

55c. 27 kJ/mol

55d. 2×10^{-5}

57. $1.36 \times 10^3 \text{ K}$

59. 6.0×10^{-4}

61. $\approx 650 \text{ K}$

63a. 0.014

63b. 329 K

65. -206.1 kJ/mol

67a. $+152.1 \text{ kJ/mol}$

67b. $\Delta G^\circ = -362.3 \text{ kJ/mol}$. The reaction is spontaneous.

69. $\Delta G^\circ = 1.7 \text{ kJmol}^{-1}$. The reaction is not spontaneous.

Integrative and Advanced Exercises

72a. True

72b. False

72c. False

72d. True

73. $0.210 \text{ mol Br}_2, 0.210 \text{ mol Cl}_2, 0.580 \text{ mol BrCl}$.

77. $2.01 \times 10^3 \text{ K}$

81. 3.70 atm

83. 297 K

86. 647 K

87. 4.2 mg AgBr/L

91a. In the solid as the temperature increases, so do the translational, rotational, and vibrational degrees of freedom. In the liquid, most of the vibrational degrees of freedom are saturated and only translational and rotational degrees of freedom can increase. In the gas phase, all degrees of freedom are saturated.

91b. The increase in translation and rotation on going from solid to liquid is much less than on going from liquid to gas.

Feature Problems

93a. $+8.556 \text{ kJ/mol}$

93b. 0.0317 bar

93c. 23.8 mmHg

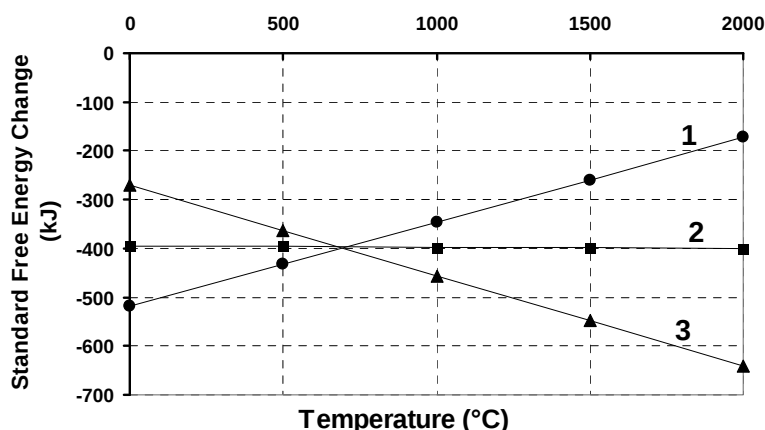
93d. 23.8 mmHg

94a. When we combine two reactions and obtain the overall value of ΔG° , we subtract the value on the plot of the reaction that becomes a reduction from the value on the plot of the reaction that is an oxidation. Thus, to reduce ZnO with elemental Mg, we subtract the values on the line labeled “ $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$ ” from those on the line labeled “ $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ ”. The result for the overall ΔG° will always be negative because every point on the “zinc” line is above the corresponding point on the “magnesium” line

94b. The “carbon” line is only below the “zinc” line at temperatures above about 1000°C . Thus, only at these elevated temperatures can ZnO be reduced by carbon.

94c. The decomposition of zinc oxide to its elements is the reverse of the plotted reaction, the value of ΔG° for the decomposition becomes negative, and the reaction becomes spontaneous, where the value of ΔG° for the plotted reaction becomes positive. This occurs above about 1850°C .

94d. The “carbon” line has a negative slope, indicating that carbon monoxide becomes more stable as temperature rises. The point where CO(g) would become less stable than $2\text{C}(\text{s})$ and $\text{O}_2(\text{g})$ looks to be below -1000°C (by extrapolating the line to lower temperatures). Based on this plot, it is not possible to decompose CO(g) to C(s) and $\text{O}_2(\text{g})$ in a spontaneous reaction.



94e.

All three lines are straight-line plots of ΔG° vs. T following the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The slope of each line multiplied by minus one is equal to the ΔS° for the oxide formation reaction. The slopes for these lines differ so markedly because these three reactions have quite different ΔS° values.

94f. Carbon would appear to be an excellent reducing agent, therefore, because it will reduce virtually any metal oxide to its corresponding metal as long as the temperature chosen for the reaction is higher than the threshold temperature.

97a. $5.8 \text{ JK}^{-1}\text{mol}^{-1}$

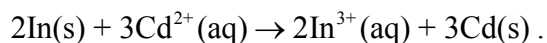
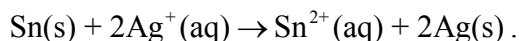
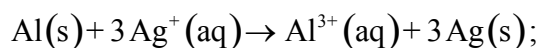
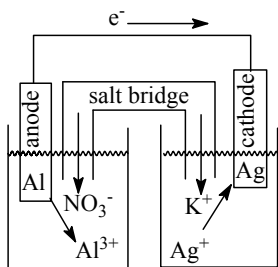
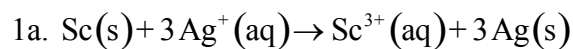
97b. $3.4 \text{ JK}^{-1}\text{mol}^{-1}$

Self-Assessment Exercises

101. The answer is (d).
102. The answer is (c).
103. The answer is (a).
104. The answer is (b).
105. The answers are (a) and (d).
- 106a. 113.6 °C
- 106b. $\Delta G^\circ = \text{zero}$.
- 107a. No reaction is expected.
- 107b. The forward reaction should occur, to some extent.
- 107c. The forward reaction should occur to a significant extent.
- 108a. Entropy change must be accessed for the system and its surroundings (ΔS_{univ}), not just for the system alone.
- 108b. Equilibrium constant can be calculated from ΔG° ($\Delta G^\circ = -RT \ln K$), and K permits equilibrium calculations for nonstandard conditions.
- 109a. 57°C
- 109b. 2.8 kJmol⁻¹
- 109c. Because $\Delta G_{\text{vap}, 298\text{K}}^\circ > 0$, the vapor pressure is less than 1 atm at 298 K, consistent with $T_{\text{bp}} = 57^\circ\text{C}$.
- 110a. Exothermic
- 110b. -186.1 kJmol⁻¹
- 110c. 4.1×10^{32}
- 110d. The reaction will be spontaneous at all temperatures.
111. Diagram (a).
112. Carbon dioxide is a gas at room temperature. The melting point of carbon dioxide is expected to be very low. At room temperature and normal atmospheric pressure this process is spontaneous. The entropy of the universe is positive.

Chapter 20 Answers

Practice Examples



3a. $+0.587\text{ V}$

3b. $+0.74\text{ V}$

4a. -0.48 V

4b. -0.424 V

5a. -1587 kJ

5b. $+1.229\text{ V}$

6a. Silver ion is one example. $E_{\text{cell}}^{\circ} = +0.460\text{ V}$.

6b. The method is not feasible because another reaction occurs that has a more positive cell potential, i.e., Na(s) reacts with water to form $\text{H}_2(\text{g})$ and NaOH(aq) .

7a. Not be a feasible method.

7b. The standard cell potential for reaction (2) is more positive than that for situation (1). Thus, reaction (2) should occur preferentially. Also, if $\text{Sn}^{4+}(\text{aq})$ is formed, it should react with Sn(s) to form $\text{Sn}^{2+}(\text{aq})$ spontaneously.

8a. The size of the equilibrium constant indicates that this reaction indeed will go to essentially 100% to completion.

8b. The equilibrium constant's small size indicates that this reaction will not go to completion.

9a. +1.815 V

9b. +0.017 V

10a. Yes

10b. 0.0150

11a. +0.23 V

11b. 6.9×10^{-9}

12a. $\text{I}_2(\text{s})$ and $\text{H}_2(\text{g})$.

12b. Silver metal $\text{Ag}^+(\text{aq})$.

13a. 1.89 amperes

13b. 5.23 h

Integrative Example

A. 0.137 V

B. (a) Oxidation: $\text{Al}(\text{s}) + 4\text{OH}^-(\text{aq}) \rightarrow [\text{Al}(\text{OH})_4]^- + 3\text{e}^-$, Reduction: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$, Overall: $4\text{Al}(\text{s}) + 4\text{OH}^-(\text{aq}) + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4[\text{Al}(\text{OH})_4]^- (\text{aq})$. (b) -2.329 V ; (c) -1303 kJ/mol ; (d) 13.4 g.

Exercises

1a. $0.340 \text{ V} < E^\circ < 0.800 \text{ V}$.

1b. $-0.440 \text{ V} < E^\circ < 0.000 \text{ V}$.

3. +0.755 V

5. -2.31 V

7a. The largest positive cell potential will be obtained for the reaction involving the oxidation of $\text{Al}(\text{s})$ to $\text{Al}^{3+}(\text{aq})$ and the reduction of $\text{Ag}^+(\text{aq})$ to $\text{Ag}(\text{s})$, $E_{\text{cell}}^\circ = 2.476 \text{ V}$.

7b. The cell with the smallest positive cell potential will be obtained for the reaction involving the oxidation of Zn(s) to $\text{Zn}^{2+}(\text{aq})$ (anode) and the reduction of $\text{Cu}^{+2}(\text{aq})$ to Cu(s) (cathode), $E_{\text{cell}}^{\circ} = 1.103 \text{ V}$.

9a. Ni^{2+}

9b. Cd

11a. Spontaneous

11b. Nonspontaneous

11c. Nonspontaneous

11d. Spontaneous

13a. Significant extent.

13b. Significant extent.

13c. Large extent.

13d. Significant extent.

13e. Not to a significant extent.

15a. Yes

15b. Yes

15c. No

17a. $3\text{Ag(s)} + \text{NO}_3^{-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) \rightarrow 3\text{Ag}^{+}(\text{aq}) + \text{NO(g)} + 2\text{H}_2\text{O(l)}$

17b. $\text{Zn(s)} + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$

17c. Does not react.

19a. $2\text{Al(s)} + 3\text{Sn}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Sn(s)}$, $E_{\text{cell}}^{\circ} = +1.539 \text{ V}$.

19b. $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^{+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag(s)}$, $E_{\text{cell}}^{\circ} = +0.029 \text{ V}$.

19c. $3\text{Cr(s)} + 2\text{Au}^{3+}(\text{aq}) \rightarrow 3\text{Cr}^{2+}(\text{aq}) + 2\text{Au(s)}$, $E_{\text{cell}}^{\circ} = 2.42 \text{ V}$.

19d. $\text{H}_2\text{O(l)} \rightarrow \text{H}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})$, $E_{\text{cell}}^{\circ} = -0.828 \text{ V}$

23a. $E_{\text{cell}}^{\circ} = -0.029 \text{ V}$, nonspontaneous.

23b. $E_{\text{cell}}^{\circ} = +0.291 \text{ V}$, spontaneous.

23c. $E_{\text{cell}}^{\circ} = -0.435 \text{ V}$, nonspontaneous.

23d. $E_{\text{cell}}^{\circ} = -0.435 \text{ V}$, nonspontaneous.

25a. $-1.165 \times 10^3 \text{ kJ}$

25b. -268 kJ

25c. $-3.1 \times 10^2 \text{ kJ}$

27a. -0.100 V

27b. 48.24 kJmol^{-1}

27c. 3.5×10^{-9}

27d. Since K is very small the reaction will not go to completion.

29a. No

29b. To the left towards reactants.

31. 1.591 V

33. 0.923 V

35. $5 \times 10^{-6} \text{ M}$

37a. 1.249 V

37b. $+0.638 \text{ V}$

39a. The reactions for which E depends on pH are those that contain either $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ in the balanced half-equation.

39b. $\text{H}^+(\text{aq})$ will inevitably be on the left side of the reduction of an oxoanion because reduction is accompanied by not only a decrease in oxidation state, but also by the loss of oxygen atoms. These oxygen atoms appear on the right-hand side as H_2O molecules. The hydrogens that are added to the right-hand side with the water molecules are then balanced with $\text{H}^+(\text{aq})$ on the left-hand side.

39c. If a half-reaction with $\text{H}^+(\text{aq})$ ions present is transferred to basic solution, it may be re-balanced by adding to each side $\text{OH}^-(\text{aq})$ ions equal in number to the $\text{H}^+(\text{aq})$ originally present. This results in $\text{H}_2\text{O}(\text{l})$ on the side that had $\text{H}^+(\text{aq})$ ions (the left side in this case) and $\text{OH}^-(\text{aq})$ ions on the other side (the right side.)

41a. 6×10^{-38} M

41b. The reaction goes to completion.

43a. +0.818 V

43b. In the standard half-cell, $[\text{OH}^-] = 1.00$ M, while in the anode half-cell in the case at hand, $[\text{OH}^-] = 0.65$ M. The forward reaction (dilution of H^+) should be even more spontaneous, (i.e. a more positive voltage will be created), with 1.00 M KOH than with 0.65 M KOH. We expect that E°_{cell} (1.000 M NaOH) should be a little larger than E_{cell} (0.65 M NaOH), which, is in fact, the case.

45. 0.177 V

47a. 0.039 V

47b. Decrease

47c. 0.025 V

47d. 0.237 M

47e. $[\text{Sn}^{2+}] = 0.50$ M, $[\text{Pb}^{2+}] = 0.18$ M.

49. $E^\circ_{\text{cell}} = -0.03$ V, therefore the reaction will not be spontaneous under standard conditions. $\text{Cl}_2(\text{g})$ could be obtained by driving it to the product side with an external voltage or, since E°_{cell} is only slightly negative, by removing products as they are formed and replenishing reactants as they are consumed.

51a. Cell diagram: $\text{Cr}(\text{s})|\text{Cr}^{2+}(\text{aq}), \text{Cr}^{3+}(\text{aq})||\text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq})|\text{Fe}(\text{s})$.

51b. +1.195 V

53a. 1.229 V

53b. +1.992 V

53c. +2.891 V

55. Calculate the quantity of charge transferred when 1.00 g of metal is consumed in each cell. The aluminum-air cell has the highest value (1.07×10^4 C).

57. Cell diagram: $\text{Li}(\text{s})|\text{Li}^+(\text{aq})|\text{KOH}(\text{satd})|\text{MnO}_2(\text{s}), \text{Mn}(\text{OH})_3(\text{s})|, E^\circ_{\text{cell}} = 2.84$ V.

59a. Oxidation of iron metal to $\text{Fe}^{2+}(\text{aq})$ should be enhanced in the body of the nail (blue precipitate), and hydroxide ion should be produced in the vicinity of the copper wire (pink color), which serves as the cathode.

59b. A scratch tears the iron and exposes “fresh” metal, which makes it is more susceptible to corrosion. We expect blue precipitate in the vicinity of the scratch.

59c. Zinc should protect the iron nail from corrosion. There should be almost no blue precipitate; the zinc corrodes instead. The pink color of OH should continue to form.

61. One way to retard oxidation of the metal would be to convert it into a cathode. Once transformed into a cathode, the metal would develop a positive charge and no longer release electrons (or oxidize). This change in polarity can be accomplished by hooking up the metal to an inert electrode in the ground and then applying a voltage across the two metals in such a way that the inert electrode becomes the anode and the metal that needs protecting becomes the cathode. This way, any oxidation that occurs will take place at the negatively charged inert electrode rather than the positively charged metal electrode.

63a. 3.3 g Zn

63b. 0.90 g Al

63c. 11 g Ag

63d. 2.9 g Ni

65a. Requires electrolysis with an applied voltage greater than +1.229V .

65b. Spontaneous

65c. Requires electrolysis with an applied voltage greater than +0.236V .

65d. Requires electrolysis with an applied voltage greater than +0.183V .

67a. $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$.

67b. $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$, $E_{\text{cell}}^{\circ} = -1.229\text{ V}$.

69a. 1.62 g Zn

69b. 20.2 min

71. 1079 C

71b. 0.7642 A

73a. Copper

73b. 37%

Integrative and Advanced Exercises

75. -0.255 V

77a. $9.38 \times 10^6 \text{ kJ}$

77b. $2.61 \times 10^3 \text{ kWh}$

80. $6.9 \times 10^{-4} \text{ M}$

82. $+127.3 \text{ kJ}$

87. 1.146 V

90. 0.051%

92. The standard hydrogen electrode is the anode. $E = 0.223 \text{ V}$.

96a. Aluminum

96b. $2 \text{ Al(s)} + 3 \text{ Ag}_2\text{S(s)} \longrightarrow 6 \text{ Ag(s)} + 2 \text{ Al}^{3+}(\text{aq}) + 3 \text{ S}^{2-}(\text{aq})$

96c. The dissolved $\text{NaHCO}_3(\text{s})$ serves as an electrolyte. It would also enhance the electrical contact between the two objects.

96d. There are several chemicals involved: Al , H_2O , and NaHCO_3 . Although the aluminum plate will be consumed very slowly because silver tarnish is very thin, it will, nonetheless, eventually erode away.

99. $Q = 1.61$, $\Delta H^\circ = -26.8 \text{ kJ}$, $\Delta S^\circ = 189.2 \text{ JK}^{-1}$, $K(\text{at } 25^\circ\text{C}) = 3.77 \times 10^{14}$,
 $K(\text{at } 50^\circ\text{C}) = 1.59 \times 10^{14}$.

100. 2.26 V

Feature Problems

102a. Equation 1: $\text{Na(s)} \rightarrow \text{Na(amalgam, 0.206\%)}$; Equation 2:

$2 \text{ Na(amalgam, 0.206 \%)} + 2 \text{ H}^+(\text{aq, 1 M}) \rightarrow 2 \text{ Na}^+(\text{1 M}) + \text{H}_2(\text{g, 1 atm})$.

102b. $\Delta G_1 = 8.156 \times 10^4 \text{ J}$, $\Delta G_2 = -36.033 \times 10^4 \text{ J}$.

102c. $2 \text{ Na(s)} + 2 \text{ H}^+(\text{aq}) \rightarrow 2 \text{ Na}^+(\text{1 M}) + \text{H}_2(\text{g, 1 atm})$, $\Delta G^\circ = -52.345 \times 10^4 \text{ J}$.

102d. $E_{\text{cell}}^\circ = 2.713 \text{ V}$, $E^\circ \{ \text{Na}^+(\text{1 M}) / \text{Na(s)} \} = -2.713 \text{ V}$

104a. $2.66 \times 10^{-13} \text{ F}$

104b. $2.26 \times 10^{-14} \text{ C}$

104c. 1.41×10^5 K^+ ions

104d. 9.3×10^{11} ions

104e. 1.5×10^{-7} ($\sim 0.000015\%$)

105. Reactions with a positive cell potential are reactions for which $\Delta G^\circ < 0$, or reactions for which $K > 1$. ΔS° , ΔH° and ΔU° cannot be used alone to determine whether a particular electrochemical reaction will have a positive or negative value.

106. $E^\circ_{\text{X}^+/\text{X}} < 0 \text{ V}$, $E^\circ_{\text{X}^+/\text{X}} > E^\circ_{\text{Y}^{2+}/\text{Y}}$.

107. Proceed similarly to the solution for 20.100.

Self-Assessment Exercises

111a. False

111b. False

111c. True

111d. True

111e. True

111f. False

111g. True

112. The correct answer is (b).

113. The correct answer is (d).

114. The correct answer is (c).

115. The correct answer is (a).

116. The correct answer is (d).

117. The correct answer is (a).

118. $\text{Zn(s)} | \text{Zn}^{2+}(1\text{M}) || \text{H}^+(1\text{M}), \text{NO}_3^-(1\text{M}) | \text{NO(g, 1atm)} | \text{Pt(s)}$, $E^\circ_{\text{cell}} = 1.719 \text{ V}$.

119. 1.82

120a. No

120b. A net reaction occurs to the left.

121a. $\text{Fe(s)} + \text{Cu}^{2+}(1\text{M}) \rightarrow \text{Fe}^{2+}(1\text{M}) + \text{Cu(s)}$, $E^\circ_{\text{cell}} = -0.780\text{V}$, electron flow from B to A

121b. $\text{Sn}^{2+}(1\text{M}) + 2\text{Ag}^{+}(1\text{M}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Ag}(\text{s})$, $E_{\text{cell}}^{\circ} = +0.646\text{V}$, electron flow from A to B.

121c. $\text{Zn}(\text{s}) + \text{Fe}^{2+}(0.0010\text{M}) \rightarrow \text{Zn}^{2+}(0.10\text{M}) + \text{Fe}(\text{s})$, $E_{\text{cell}}^{\circ} = +0.264\text{V}$, electron flow from A to B.

122a. $\text{Cl}_2(\text{g})$ at anode and $\text{Cu}(\text{s})$ at cathode.

122b. $\text{O}_2(\text{g})$ at anode and $\text{H}_2(\text{g})$ and $\text{OH}^{-}(\text{aq})$ at cathode.

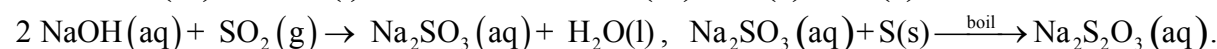
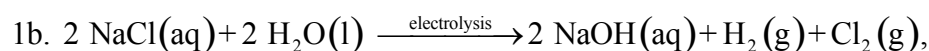
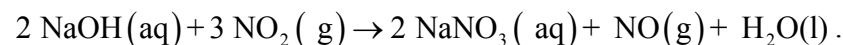
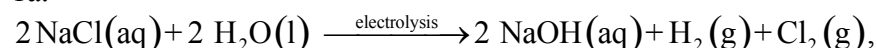
122c. $\text{Cl}_2(\text{g})$ at anode and $\text{Ba}(\text{l})$ at cathode.

122d. $\text{O}_2(\text{g})$ at anode and $\text{H}_2(\text{g})$ and $\text{OH}^{-}(\text{aq})$ at cathode.

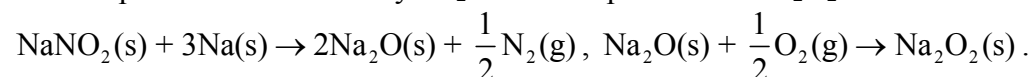
Chapter 21 Answers

Practice Examples

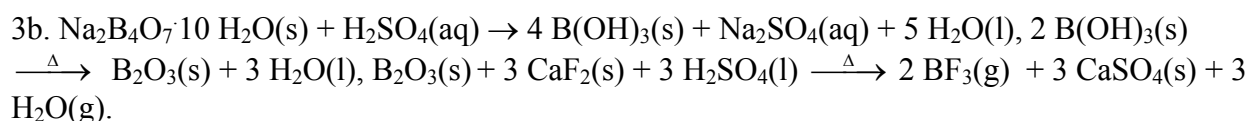
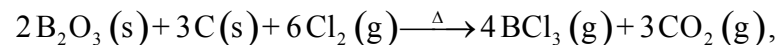
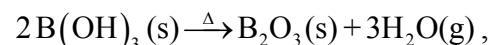
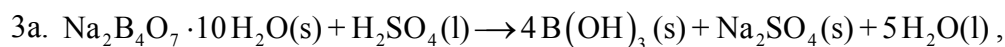
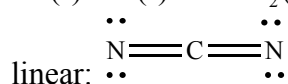
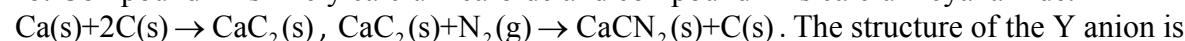
1a.



2a. Compound X is most likely Na_2O and compound Y is Na_2O_2 .



2b. Compound X is likely calcium carbide and compound Y is calcium cyanamide.



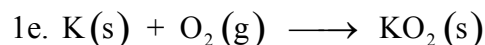
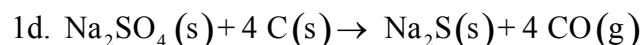
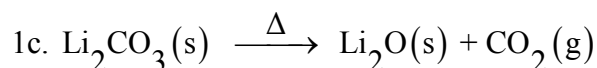
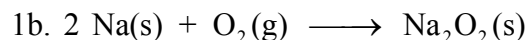
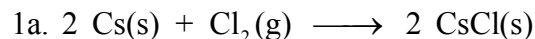
Integrative Example

A. $\text{NaCN}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{CN}^-(\text{aq})$, $\text{Al}(\text{NO}_3)_3(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{NO}_3^-(\text{aq})$. The product $[\text{Al}^{3+}][\text{OH}^-]^3 = 4.0 \times 10^{-9}$ is much greater than K_{SP} for $\text{Al}(\text{OH})_3$ (1.3×10^{-33}) and therefore precipitation will occur.

B. When $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ is heated, it decomposes to $\text{Be}(\text{OH})_2(\text{s})$, $\text{H}_2\text{O}(\text{g})$, and $\text{HCl}(\text{g})$, as discussed in Section 21-3. $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ comprises $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and Cl^- ions. Because of the high polarizing power of Be^{2+} , it is difficult to remove the coordinated water molecules by heating the solid and the acidity of the coordinated H_2O molecules is enhanced. When $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ is dissolved in water, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ ions react with water, and $[\text{Be}(\text{H}_2\text{O})_3(\text{OH})]^+$ and H_3O^+ ions are produced. Hence, a solution of $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ is expected to be acidic. When $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is heated, $\text{CaCl}_2(\text{s})$ and $\text{H}_2\text{O}(\text{g})$ are produced. Because the charge density and polarizing power of Ca^{2+} is much less than that of Be^{2+} , it is much easier to drive off the

coordinated water molecules by heating the solid. When $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in water, $\text{Ca}^{2+}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$ are produced. However, the charge density of the Ca^{2+} ion is too low to affect the acidity of water molecules in the hydration sphere of the Ca^{2+} ion. Hence, a solution of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ has a neutral pH.

Exercises



3. Both LiCl and KCl are soluble in water, but Li_3PO_4 is not very soluble. Hence the addition of $\text{K}_3\text{PO}_4(\text{aq})$ to a solution of the white solid will produce a precipitate if the white solid is LiCl, but no precipitate if the white solid is KCl. The best method is a flame test; lithium gives a red color to a flame, while the potassium flame test is violet.

5. Based on molar solubilities: $\text{MgCO}_3 < \text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3$.

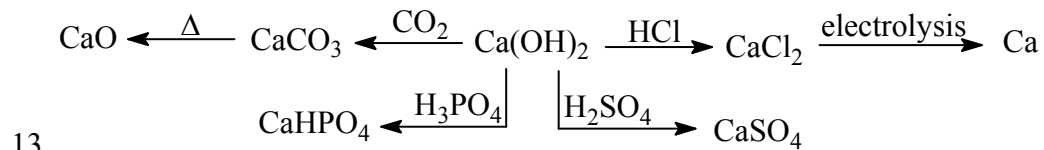
7a. 11.61

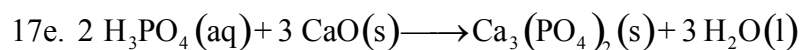
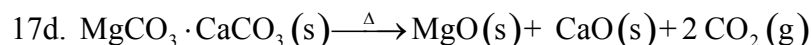
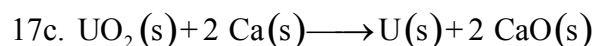
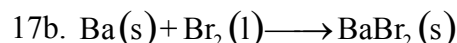
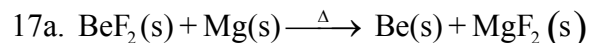
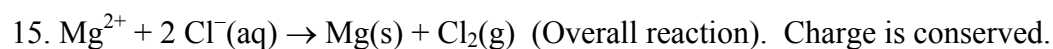
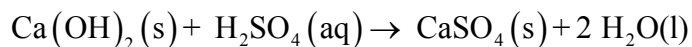
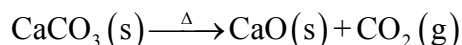
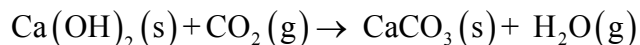
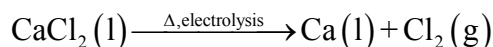
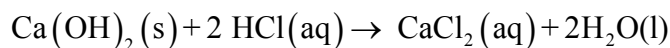
7b. As long as NaCl is in excess and the volume of the solution is nearly constant, the solution pH only depends on the number of electrons transferred.

9a. 71.5% yield

9b. NH_3 is simply used during the Solvay process to produce the proper conditions for the desired reactions. Any net consumption of NH_3 is the result of unavoidable losses during production.

11. $K = 1.87 \times 10^{-25}$. $\text{Na}_2\text{O}_2(\text{s})$ is thermodynamically stable with respect to $\text{Na}_2\text{O}(\text{s})$ and $\text{O}_2(\text{g})$ at 298 K.





19a. Equilibrium lies slightly to the left.

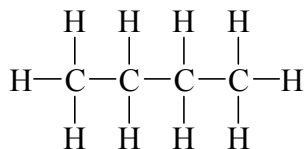
19b. Equilibrium lies to the left.

19c. Equilibrium lies to the right.

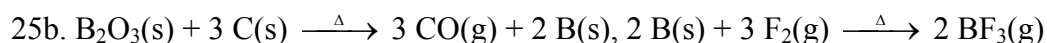
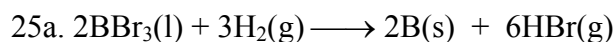
21. The SO_4^{2-} ion is a large polarizable ion. A cation with a high polarizing power will polarize the SO_4^{2-} ion and kinetically assist the decomposition to SO_3 . Because Be^{2+} has the largest charge density of the group 2 cations, we expect Be^{2+} to be the most polarizing and thus, BeSO_4 will be the least stable with respect to decomposition.

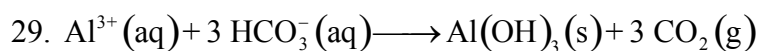
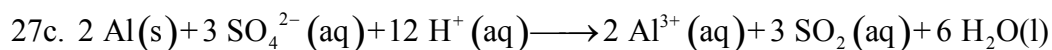
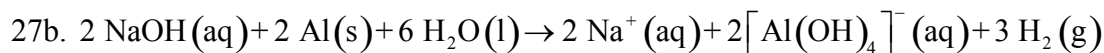
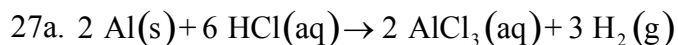
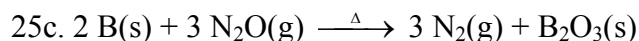
23a. B_4H_{10} contains 22 valence electrons or 11 pairs. Ten of these pairs could be allocated to form 10 B—H bonds, leaving only one pair to bond the four B atoms together. Clearly an electron deficient situation.

23b. Two



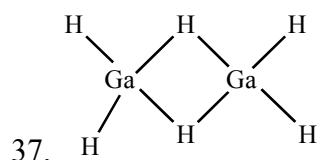
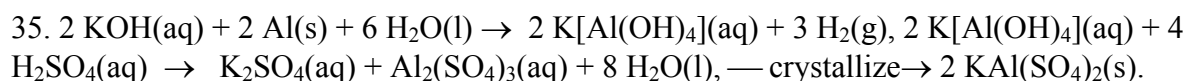
23c.



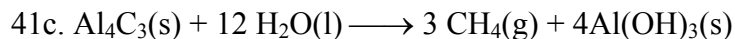
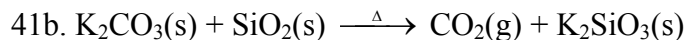
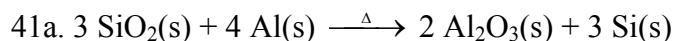


31. Aluminum and its oxide are soluble in both acid and base. Al(s) is resistant to corrosion only over the pH range 4.5 to 8.5. Thus, aluminum is inert only when the medium to which it is exposed is neither highly acidic nor highly basic.

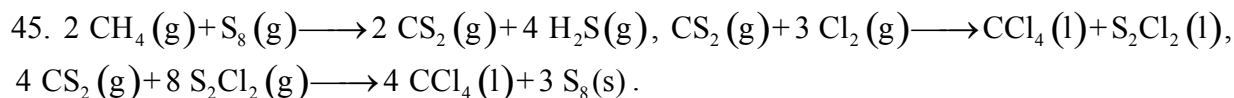
33. $[\text{Al(OH)}_4]^- \text{(aq)} + \text{CO}_2\text{(aq)} \longrightarrow \text{Al(OH)}_3\text{(s)} + \text{HCO}_3^-\text{(aq)}$. HCl(aq), being a strong acid, can't be used because it will dissolve the Al(OH)₃(s).



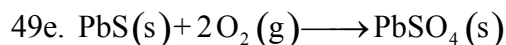
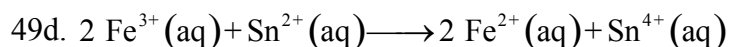
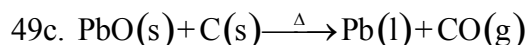
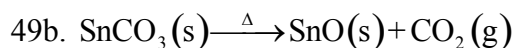
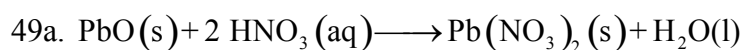
39. In the sense that diamonds react imperceptibly slowly at room temperature (either with oxygen to form carbon dioxide, or in its transformation to the more stable graphite), it is essentially true that “diamonds last forever.” However, at elevated temperatures, diamond will burn to form CO₂(g) and thus the statement is false. Eventually, the conversion to graphite occurs.



43. A silane is a silicon-hydrogen compound, with the general formula Si_nH_{2n+2}. A silanol is a compound in which one or more of the hydrogens of silane is replaced by an —OH group. Silicones are produced when silanols condense into chains, with the elimination of a water molecule between every two silanol molecules.



47. The formula is $\text{KAl}_2(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$. Since they are not segregated into O_2 units in the formula, all of the oxygen atoms in the mineral must be in the -2 oxidation state. Potassium is obviously in the $+1$ oxidation state, as are the hydrogen atoms in the hydroxyl groups. Up to this point, we have -24 from the twelve oxygen atoms and $+3$ from the potassium and hydrogen atoms for a net number of -21 for the oxidation state. We still have three aluminum atoms and three silicon atoms to account for. In oxygen-rich salts such as mica, we would expect that the silicon and the aluminum atoms would be in their highest possible oxidation states, namely $+4$ and $+3$, respectively. Since the salt is neutral, the oxidation numbers for the silicon and aluminum atoms must add up to $+21$. This is precisely the total that is obtained if the silicon and aluminum atoms are in their highest possible oxidation states: $(3 \times +3) + (3 \times +4) = +21$. Consequently, the empirical formula for white muscovite is consistent with the expected oxidation state for each element present.



51a. The reaction will go to completion.

51b. The reaction is not spontaneous.

51c. The reaction is not spontaneous.

53. PbCl_2

Integrative and Advanced Exercises.

58. $\text{:}\ddot{\text{I}}\text{---}\ddot{\text{I}}\text{---}\ddot{\text{I}}\text{:}$. The Li^+ ion has a high charge density and significant polarizing power. The Li^+ ion will polarize the I_3^- to a significant extent and presumably assists the decomposition of I_3^- to I_2 and I^- .

59. $K = P_{\text{O}_2} = 8.8 \times 10^4$.

62a. 0.332 g MgO

62b. If the mass of product formed from the starting Mg differs from the 0.332 g MgO predicted, then the product could be a mixture of magnesium nitride and magnesium oxide. This scenario is not implausible since molecular nitrogen is readily available in the atmosphere.

62c. The product is 69% by mass MgO.

63a. Since Li has a higher boiling point (1347°C) than K (773.9°C), a reaction similar to (21.4) is not a feasible way of producing Li metal from LiCl.

63b. Cs has a lower boiling point (678.5°C) than K (773.9°C), and thus a reaction similar to (21.4) is a feasible method of producing Cs metal from CsCl.

64a. -852 kJ

64b. $4 \text{ Al(s)} + 3 \text{ MnO}_2\text{(s)} \rightarrow 2 \text{ Al}_2\text{O}_3\text{(s)} + 3 \text{ Mn(s)}$, $\Delta H = -1792 \text{ kJ}$.

64c. $2 \text{ Al(s)} + 3 \text{ MgO(s)} \rightarrow \text{Al}_2\text{O}_3\text{(s)} + 3 \text{ Mg(s)}$, $\Delta H = +129 \text{ kJ}$.

66. Mg(OH)_2 should precipitate.

67a. 81.4 ppm Ca^{2+}

67b. 48.7 g CaO

67c. Use the K_{sp} expression for CaCO_3 to determine the needed $[\text{CO}_3^{2-}]$. The carbonate ion concentration can readily be achieved by adding solid Na_2CO_3 .

67d. $2.2 \times 10^2 \text{ g Na}_2\text{CO}_3$

68a. $2.68 \times 10^5 \text{ g Al}$

68b. 1.3 metric tons of coal .

69. -1.605 V. If the oxidation of C(s) to $\text{CO}_2\text{(g)}$ did not occur, then the cell reaction would just be the reverse of the formation reaction of Al_2O_3 with $n = 6 \text{ e}^-$. $E^\circ = \Delta E^\circ = -2.626 \text{ V}$.

70. 19 g $\text{Pb(NO}_3)_2$

73a. $7.4 \times 10^{-3} \text{ M}$

73b. $6.4 \times 10^{-4} \text{ M}$

73c. $2.0 \times 10^{-3} \text{ M}$

76. We would expect MgO(s) to have a larger value of lattice energy than MgS(s) because of the smaller interionic distance in MgO(s) . Lattice energy of $\text{MgO} = -3789 \text{ kJ}$, Lattice energy of $\text{MgS} = -3215 \text{ kJ}$.

77. The empirical formula is M_3C_{60} , $n = 3$.

Feature Problems

78a. $\Delta H^\circ = -277 \text{ kJ} \approx \Delta G^\circ$, $E_{\text{red}}^\circ = -2.87 \text{ V}$.

78b. $E_{\text{red}}^\circ = -3.03 \text{ V}$.

Self-Assessment Exercises

83. The answer is (c).

84. The answer is (f).

85a. $\text{BCl}_3\text{NH}_3(\text{g})$ (an adduct)

85b. $\text{KO}_2(\text{s})$

85c. $\text{Li}_2\text{O}(\text{s})$

85d. $\text{Ba}(\text{OH})_2(\text{aq})$ and $\text{H}_2\text{O}_2(\text{aq})$.

86. The thermite reaction is evidence that aluminum will readily extract oxygen from Fe_2O_3 . Aluminum can be used for making products that last and for structural purposes, because aluminum develops a coating of Al_2O_3 that protects the metal beneath it.

87. The answer is (b).

88a. $\text{Li}_2\text{CO}_3(\text{s}) \xrightarrow{\Delta} \text{Li}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$

88b. $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \longrightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

88c. $2\text{Al}(\text{s}) + 2\text{NaOH}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Na}[\text{Al}(\text{OH})_4](\text{aq}) + 3\text{H}_2(\text{g})$

88d. $\text{BaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ba}(\text{OH})_2(\text{aq, limited solubility})$

88e. $2\text{Na}_2\text{O}_2(\text{s}) + 2\text{CO}_2(\text{g}) \longrightarrow 2\text{Na}_2\text{CO}_3(\text{s}) + \text{O}_2(\text{g})$

89a. $\text{MgCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \longrightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

89b. $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$ followed by the reaction in Exercise 82(c).

89c. $2\text{NaCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{concd., aq}) \xrightarrow{\Delta} \text{Na}_2\text{SO}_4(\text{s}) + 2\text{HCl}(\text{g})$

90a. $\text{K}_2\text{CO}_3(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \longrightarrow \text{BaCO}_3(\text{s}) + 2\text{KOH}(\text{aq})$

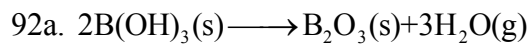
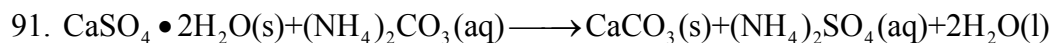
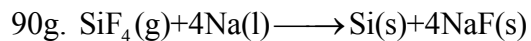
90b. $\text{Mg}(\text{HCO}_3)_2(\text{aq}) \xrightarrow{\Delta} \text{MgCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

90c. $\text{SnO}(\text{s}) + \text{C}(\text{s}) \xrightarrow{\Delta} \text{Sn}(\text{l}) + \text{CO}(\text{g})$

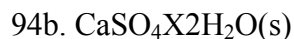
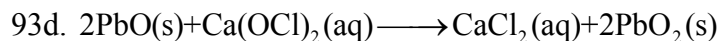
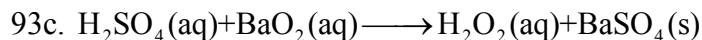
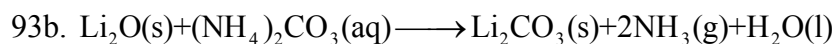
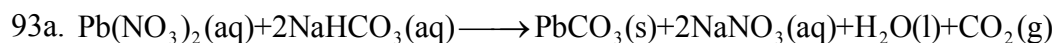
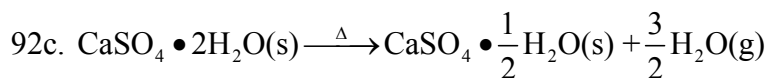
90d. $\text{CaF}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{concd. aq}) \xrightarrow{\Delta} \text{CaSO}_4(\text{s}) + 2\text{HF}(\text{g})$

90e. $\text{NaHCO}_3(\text{s}) + \text{HCl}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

90f. $\text{PbO}_2(\text{s}) + 4\text{HBr}(\text{aq}) \longrightarrow \text{PbBr}_2(\text{s}) + \text{Br}_2(\text{l}) + 2\text{H}_2\text{O}(\text{l})$



92b. No reaction.



94c. $\text{BaSO}_4(\text{s})$ in water.

94d. $\text{Al}_2\text{O}_3(\text{s})$ with Fe^{3+} and Ti^{4+} replacing some Al^{3+} in the crystal structure.

95. $1.27 \times 10^3 \text{ m}^3$

Chapter 22 Answers

Practice Examples

1a. 0.622 V

1b. 1.453 V

2a. 1.7×10^{-48}

2b. $K_p = 4 \times 10^{-34}$. 4×10^{-15} % decomposed.

Integrative Example

A. E° for the disproportionation reaction is negative. The disproportionation of NO_2^- to NO_3^- and NO is not spontaneous.

B. E_{cell}° for the reaction is positive and therefore disproportionation of HNO_2 to NO_3^- and NO is spontaneous under standard conditions.

Exercises

1. LiF, BeF_2 , BF_3 , CF_4 , NF_3 , OF_2 . LiF is an ionic compound, BeF_2 is a network covalent compound, and the others are molecular covalent compounds.

3. Bi_2O_3 is most basic, P_4O_6 is least basic (and is actually acidic), and Sb_4O_6 is amphoteric.

5. 7.8×10^5 L air

7a. Trigonal pyramidal

7b. Tetrahedral

7c. Square pyramidal

9. $3 \text{XeF}_4(\text{aq}) + 6 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Xe}(\text{g}) + 3/2 \text{O}_2(\text{g}) + 12 \text{HF}(\text{g}) + \text{XeO}_3(\text{s})$

11. The bond energy of the noble gas fluorine is too small to offset the energy required to break the F—F bond.

13. Iodide ion is slowly oxidized to iodine, which is yellow-brown in aqueous solution, by oxygen in the air: $4\text{I}^-(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \longrightarrow 2\text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$.

15. Displacement reactions involve one element displacing another element from solution. The element that dissolves in the solution is more “active” than the element supplanted from solution. Within the halogen group, the activity decreases from top to bottom. Thus, each halogen is able to displace the members of the group below it, but not those above it. The only halogen with sufficient oxidizing power to displace $\text{O}_2(\text{g})$ from water is $\text{F}_2(\text{g})$. None of the halogens reacts with water to form $\text{H}_2(\text{g})$.

17a. 2×10^6 kg F_2

17b. Since there is no chemical oxidizing agent that is stronger than $F_2(g)$, this method of displacement would not work for $F_2(g)$.

19. $6 Cl_2(aq) + 6 H_2O(l) \rightarrow 2 ClO_3^-(aq) + 12 H^+(aq) + 10 Cl^-(aq)$, $E^\circ_{cell} = -0.095$ V. Since the final cell voltage is negative, the disproportionation reaction will not occur spontaneously under standard conditions.

21a. T-shaped

21b. Square pyramidal

21c. Square planar

23a. 0.085 V

23b.

25a. $2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$

25b. $2KClO_4(s) \xrightarrow{\Delta} 2KClO_3(s) + O_2(g)$

27. CO_2

29. 3×10^{-5} mmHg

31. The electrolysis reaction is $2H_2O(l) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$. In this reaction, 2 moles of $H_2(g)$ are produced for each mole of $O_2(g)$. By the law of combining volumes, we would expect the volume of hydrogen to be twice the volume of oxygen produced.

33. 5.89

35. 302 kJ / mol

37a. H_2S , while polar, forms only weak hydrogen bonds. H_2O forms much stronger hydrogen bonds, leading to a higher boiling point.

37b. All electrons are paired in O_3 , producing a diamagnetic molecule.

39a. $K_{eq} = 3.2 \times 10^{41}$, the reaction goes to completion.

39b. $K_{eq} = 2.1 \times 10^{-65}$, the reaction does not even come close to going to completion.

39c. $K_{eq} = 9.0 \times 10^2$, the reaction goes to completion.

39d. $K_{eq} = 4.8 \times 10^{-7}$, the reaction does not even come close to going to completion.

41. 30 L

43a. zinc sulfide

43b. potassium hydrogen sulfite

43c. potassium thiosulfate

43d. sulfur tetrafluoride

45a. $\text{FeS(s)} + 2 \text{HCl(aq)} \longrightarrow \text{FeCl}_2\text{(aq)} + \text{H}_2\text{S(aq)}$ MnS(s) , ZnS(s) , etc. also are possible.

45b. $\text{CaSO}_3\text{(s)} + 2 \text{HCl(aq)} \longrightarrow \text{CaCl}_2\text{(aq)} + \text{H}_2\text{O(l)} + \text{SO}_2\text{(g)}$

45c. $\text{SO}_2\text{(aq)} + \text{MnO}_2\text{(s)} \longrightarrow \text{Mn}^{2+}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)}$

45d. $\text{S}_2\text{O}_3^{2-}\text{(aq)} + 2 \text{H}^+\text{(aq)} \longrightarrow \text{S(s)} + \text{SO}_2\text{(g)} + \text{H}_2\text{O(l)}$

47. The decomposition of thiosulfate ion is more highly favored in an acidic solution. If the white solid is Na_2SO_4 , there will be no reaction with strong acids such as HCl . By contrast, if the white solid is $\text{Na}_2\text{S}_2\text{O}_3$, $\text{SO}_2\text{(g)}$ will be liberated and a pale yellow precipitate of S(s, rhombic) will form upon addition of HCl(aq) . $\text{S}_2\text{O}_3^{2-}\text{(aq)} + 2 \text{H}^+\text{(aq)} \longrightarrow \text{S(s)} + \text{SO}_2\text{(g)} + \text{H}_2\text{O(l)}$.

49. 1.21

51. 7.002%

53a. +4

53b. +5

53c. -2

53d. +4

55a. $\text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)} \rightleftharpoons 2 \text{NH}_3\text{(g)}$

55b. $4 \text{NH}_3\text{(g)} + 5 \text{O}_2\text{(g)} \xrightarrow{850^\circ\text{C, Pt}} 4 \text{NO(g)} + 6 \text{H}_2\text{O(g)}$

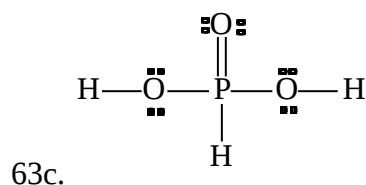
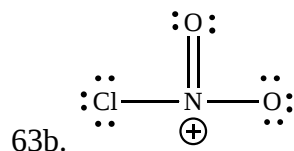
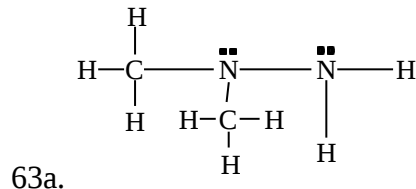
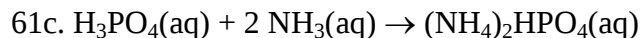
55c. $2 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}$, $3 \text{NO}_2\text{(g)} + \text{H}_2\text{O(l)} \rightarrow 2 \text{HNO}_3\text{(aq)} + \text{NO(g)}$.

57. $2 \text{Na}_2\text{CO}_3\text{(aq)} + 4 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 4 \text{NaNO}_2\text{(aq)} + 2 \text{CO}_2\text{(g)}$

59. $6 \times 10^9 \text{ kg}$

61a. $2 \text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$

61b. $\text{HNO}_2\text{(aq)} + \text{N}_2\text{H}_5^+\text{(aq)} \rightarrow \text{HN}_3\text{(aq)} + 2 \text{H}_2\text{O(l)} + \text{H}^+\text{(aq)}$, $\text{HN}_3\text{(aq)} + \text{HNO}_2\text{(aq)} \rightarrow \text{N}_2\text{(g)} + \text{H}_2\text{O(l)} + \text{N}_2\text{O(g)}$.



65a. hydrogen phosphate ion

65b. calcium pyrophosphate or calcium diphosphate

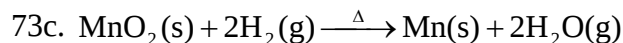
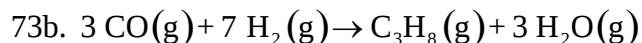
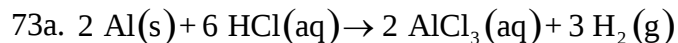
65c. tetrapolyphosphoric acid

67. 1.031 V

69a. Nitrogen atom cannot bond to five fluorine atoms because, as a second-row element, it cannot accommodate more than four electron pairs.

69b. The NF_3 molecule is trigonal pyramidal. The lone pair on the N atom causes the F—N—F bond angle to decrease from the ideal tetrahedral bond angle of 109° to 102.5° .

71. $\text{CH}_4(\text{g})$, $\Delta H^\circ_{\text{combustion}} = -890.3 \text{ kJ}$; $\text{C}_2\text{H}_6(\text{g})$, $\Delta H^\circ_{\text{combustion}} = -1559.7 \text{ kJ}$; $\text{C}_3\text{H}_8(\text{g})$, $\Delta H^\circ_{\text{combustion}} = -2219.9 \text{ kJ}$; $\text{C}_4\text{H}_{10}(\text{g})$, $\Delta H^\circ_{\text{combustion}} = -2877.4 \text{ kJ}$.



75a. $\text{CaH}_2(\text{s})$ produces the most $\text{H}_2(\text{g})$.

75b. CaH_2 produces the greatest amount of H_2 per gram of solid.

77. Since CH_4 has the highest hydrogen atom to non-hydrogen atom ratio, this molecule has the greatest mass percent hydrogen.

79. NH_2^- has 8 valence electrons. The first four MO's are fully occupied. Because the $2p_x$ orbital on N is strongly bonding in the bent configuration, the energy of the NH_2^- will be much lower for the bent configuration.

Integrative and Advanced Exercises

81. In step (1), oxygen is converted to H_2O by the reaction $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$. Step (2) ensures that unreacted hydrogen from step (1) is also converted to $\text{H}_2\text{O}(\text{l})$. The dehydrated zeolite has a very strong affinity for water molecules and thus, $\text{H}_2\text{O}(\text{l})$ is removed from the gas mixture.

84. NaNO_2 decolorizes acidic solution of KMnO_4 according to the following balanced chemical equation: $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{NaNO}_2 \rightarrow 5\text{NaNO}_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O}$. NaNO_3 does not react with acidic solution of KMnO_4 .

85. 0.1716 M

86. $3.0 \times 10^{-20} \text{ J/atom}$

89. $2 \text{ NH}_4\text{ClO}_4(\text{s}) \longrightarrow \text{N}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{g}) + \text{Cl}_2(\text{g}) + 2 \text{ O}_2(\text{g})$

92. 9.23 g/cm^3

94a. 339 kJ/mol

94b. The radiation is in the near ultraviolet. $\nu = 8.50 \times 10^{14} \text{ s}^{-1}$, $\lambda = 353 \text{ nm}$.

95a. $\text{mass P} = 1.000 \text{ g P}_4\text{O}_{10} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{283.89 \text{ g P}_4\text{O}_{10}} \times \frac{4 \text{ mol P}}{1 \text{ mol P}_4\text{O}_{10}} \times \frac{30.974 \text{ g P}}{1 \text{ mol P}} = 0.436 \text{ g P}$. Thus, multiplying the mass of P_4O_{10} by 0.436 will give the mass (or mass percent) of P.

$$\begin{aligned} \text{mass Ca}_3(\text{PO}_4)_2 &= 1.000 \text{ g P}_4\text{O}_{10} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{283.89 \text{ g P}_4\text{O}_{10}} \times \frac{4 \text{ mol P}}{1 \text{ mol P}_4\text{O}_{10}} \\ &\quad \times \frac{1 \text{ mol Ca}_3(\text{PO}_4)_2}{2 \text{ mol P}} \times \frac{310.18 \text{ g Ca}_3(\text{PO}_4)_2}{1 \text{ mol Ca}_3(\text{PO}_4)_2} = 2.185 \text{ g Ca}_3(\text{PO}_4)_2 \end{aligned}$$

Thus, multiplying the mass of P_4O_{10} (283.88) by 2.185 will give the mass (or mass %) of BPL.

95b. A %BPL greater than 100% means that the material has a larger %P than does pure $\text{Ca}_3(\text{PO}_4)_2$.

95c. 92.4% BPL

99. 15 g H_2SO_4 , 37 g Cl_2 .

100. Solving for $[\text{H}^+]$ yields a value of $8 \times 10^{-5} \text{ M}$ which corresponds to a pH of 4.1. The solution is still acidic.

102. Oxidations: $\text{XeF}_4(\text{g}) + 3 \text{H}_2\text{O} \longrightarrow \text{XeO}_3(\text{g}) + 4 \text{HF}(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$,
 $2 \text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^-$. Reduction: $\text{XeF}_4(\text{g}) + 4 \text{e}^- \longrightarrow \text{Xe}(\text{g}) + 4 \text{F}^-(\text{aq})$.
 Net: $3 \text{XeF}_4(\text{g}) + 6 \text{H}_2\text{O}(\text{l}) \longrightarrow 2 \text{XeO}_3(\text{g}) + 12 \text{HF}(\text{aq}) + 3/2 \text{O}_2(\text{g}) + 2 \text{Xe}(\text{g})$

104. $[\text{HOCl}(\text{aq})] = [\text{H}^+(\text{aq})] = [\text{Cl}^-(\text{aq})] = 0.030 \text{ M}$ and $[\text{Cl}_2(\text{aq})] = 0.060 \text{ M}$.

105. 0.70 V

107. Both molecules are V shaped, with a lone pair of electrons on the central atom. For O_3 , the structure is a hybrid of two equivalent structures. In each of these structures, the central atom has a formal charge of +1. The oxygen–oxygen bond order is between 1 and 2. Although many resonance structures can be drawn for SO_2 , in the most important structure, the formal charge on the S atom is zero and the sulfur–oxygen bonds are double bonds.

109. $\Delta H_f^\circ = 639 \text{ kJ mol}^{-1}$. The formation reaction is very endothermic and thus energetically unfavorable. This result supports the observation that $\text{Xe}(\text{g})$ does not react directly with $\text{O}_2(\text{g})$ to form $\text{XeO}_3(\text{g})$. Because the reaction converts 2.5 moles of gas into 1 mole of gas, we expect $\Delta S_f^\circ < 0$; thus, the reaction is also entropically unfavorable.

Feature Problems

110. Demonstrate that the three reactions result in the decomposition of water as the net reaction: $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$. First balance each equation and then consider how to manipulate and add the equations together to get the overall equation.

112. $2 \text{H}^+(\text{aq}) + \text{ClO}_3^-(\text{aq}) + 1 \text{e}^- \rightarrow \text{ClO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$. The standard voltage for this half-reaction is given in Appendix D. $\text{H}^+(\text{aq}) + \text{ClO}_2(\text{aq}) + 1 \text{e}^- \rightarrow \text{HClO}_2(\text{g})$, $E^\circ = 1.187 \text{ V}$.

Self-Assessment Exercises

120. The answer is (b).

121. The answer is (d).

122. The answer is (c).

123. The answer is (a).

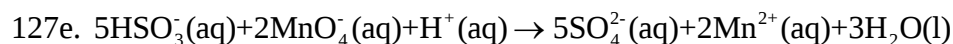
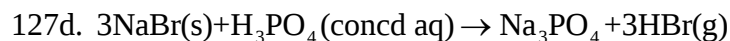
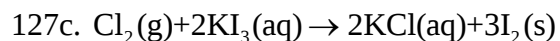
124. The answer is (d).

125. The answer is (b).

126. The answer is (a) and (b).

127a. $\text{Cl}_2(\text{g}) + 2 \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{NaOCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

127b. $2 \text{NaI}(\text{s}) + 2 \text{H}_2\text{SO}_4(\text{concd aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2 \text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g}) + \text{I}_2(\text{g})$



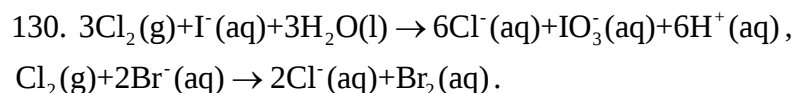
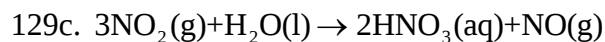
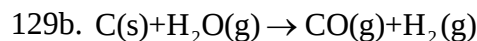
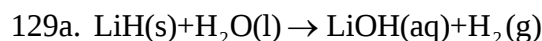
128a. $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$. A catalyst such as MnO_2 is required. Electrolysis of H_2O is an alternate method.

128b. $3\text{Cu}(\text{s}) + 8\text{H}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq}) \rightarrow 3\text{Cu}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 2\text{NO}(\text{g})$. Difficult to control reaction so that $\text{NO}(\text{g})$ is the only reduction product.

128c. $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$. A number of other metals can be used.

128d. $\text{NH}_4\text{Cl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{NH}_3(\text{g})$. Other ammonium salts and other bases work as well.

128e. $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$. Other carbonates and acids can be used.



131. 5.0 kg³ of seawater.

132a. AgAt

132b. sodium perxenate

132c. MgPo

132d. tellurous acid

132e. K_2SeSO_3

132f. potassium perastatate

133. 0.38 V

134a. SO_3

134b. SO_2

134c. Cl_2O_7

134d. I_2O_5

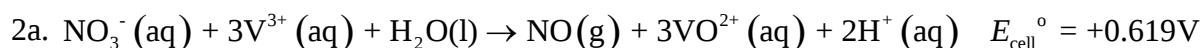
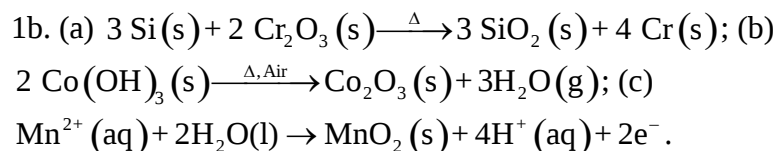
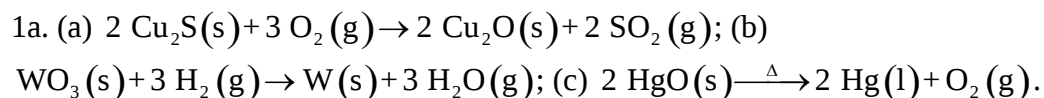
135a. False

135b. True

135c. True

Chapter 23Answers

Practice Examples



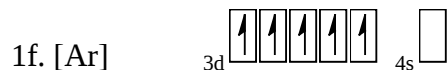
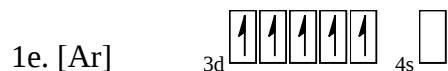
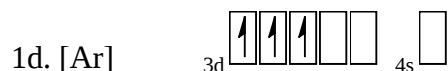
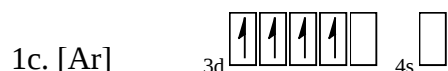
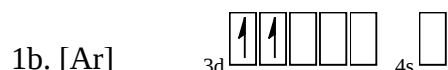
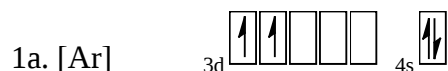
2b. $-E^\circ$ for the couple must be $> -0.041 \text{ V}$ and $< +1.13 \text{ V}$. $\text{Fe}(\text{s})$, $\text{Cr}^{2+}(\text{aq})$, and $\text{Zn}(\text{s})$ will do the job.

Integrative Example

A. $2 \text{V}^{2+} + \text{PtCl}_6^{2-} \rightarrow 2 \text{V}^{3+} + \text{PtCl}_4^{2-} + 2 \text{Cl}^-$. The formation of PtCl_6^{2-} is favored by using a very low concentration of V^{2+} and very high concentrations of V^{3+} , PtCl_4^{2-} , and Cl^- . In practical terms, an external voltage source would be required to make a significant amount of PtCl_6^{2-} from V^{3+} , PtCl_4^{2-} , and Cl^- .

B. The disproportionation reaction is $3 \text{Ti}^{2+} \rightarrow 2 \text{Ti}^{3+} + \text{Ti}$ and $E^\circ = -1.261 \text{ V}$. Because $E^\circ < 0$ the reaction is not spontaneous under standard conditions.

Exercises



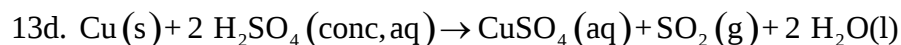
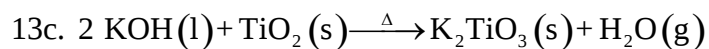
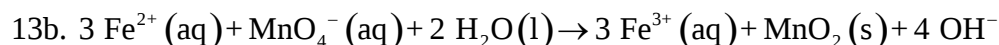
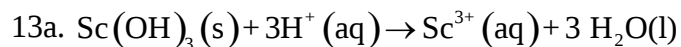
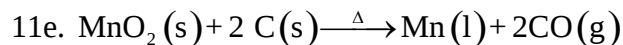
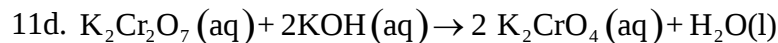
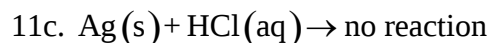
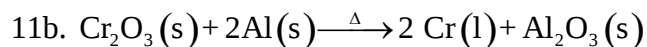
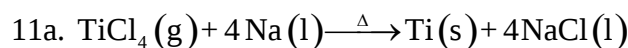
3. A given main-group metal typically displays just one oxidation state, usually equal to its family number in the periodic table. Main group metals do not form a wide variety of complex ions, with Al^{3+} , Sn^{2+} , Sn^{4+} , and Pb^{2+} being major exceptions. On the other hand, most transition metal ions form an extensive variety of complex ions. Most compounds of main group

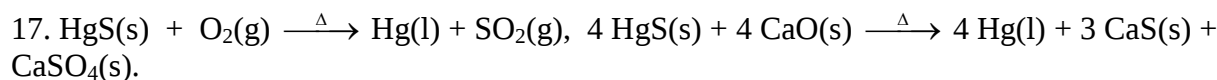
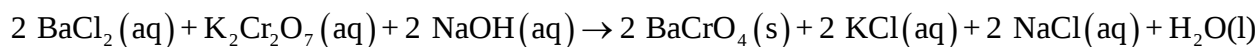
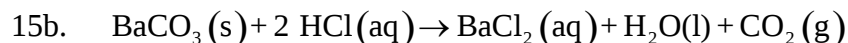
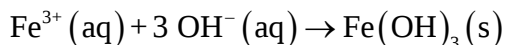
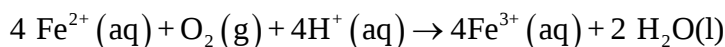
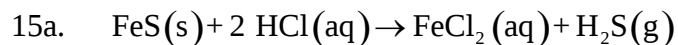
metals are colorless; exceptions occur when the anion is colored. On the other hand, many of the compounds of transition metal cations are colored, due to d-d electron transitions. Virtually every main-group metal cation has no unpaired electrons and hence is diamagnetic. On the other hand, many transition metals cations have one or more unpaired electrons and therefore are paramagnetic.

5. When an electron and a proton are added to a main group element to create the element of next highest atomic number, it is the electron that influences the radius. The electron is added to the outermost shell (n value), which is farthest from the nucleus. Moreover, the added electron is well shielded from the nucleus and hence it is only weakly attracted to the nucleus. Thus, this electron billows out and, as a result, has a major influence on the size of the atom. However, when an electron and a proton are added to a transition metal atom to create the atom of next highest atomic number, the electron it is not added to the outermost shell. The electron is added to the d -orbitals, which are one principal quantum number lower than the outermost shell. Also, the electron in the same subshell as the added electron offers little shielding. Thus it has small effect on the size of the atom.

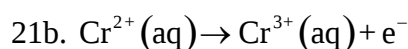
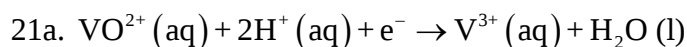
7. Manganese. One possible explanation might be its $3d^5 4s^2$ electron configuration. Removing one electron produces an electron configuration ($3d^5 4s^1$) with two half-filled subshells, removing two produces one with a half-filled and an empty subshell. Then there is no point of semistability until the remaining five d electrons are removed.

9. The greater ease of forming lanthanide cations compared to forming transition metal cations, is due to the larger size of lanthanide atoms. The valence (outer shell) electrons of these larger atoms are further from the nucleus, less strongly attracted to the positive charge of the nucleus in diffuse f -orbitals that do not penetrate effectively and are very effectively shielded by the core electrons. As a result, they are removed much more readily.





19. The graph should be similar to that for $2 \text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2 \text{MgO(s)}$. We expect a positive slope with slight changes in the slope after the melting point (839 °C) and boiling point (1484 °C), mainly owing to changes in entropy. The plot will be below the ΔG° line for $2 \text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2 \text{MgO(s)}$ at all temperatures.



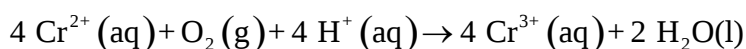
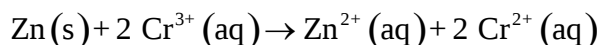
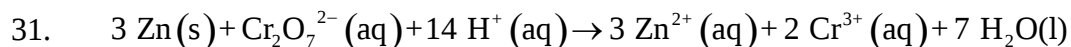
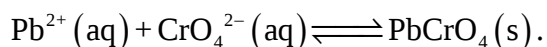
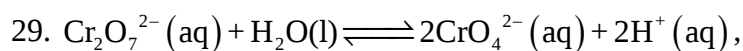
23a. $E^\circ_{\text{cell}} = -0.704\text{V}$. Does not occur to a significant extent.

23b. $E^\circ_{\text{cell}} = +0.229\text{V}$. Does occur to a significant extent.

23c. $E^\circ_{\text{cell}} = +0.54\text{V}$. Does occur to a significant extent.

25. $-E^\circ$ for the couple must be $> -0.337\text{ V}$ and $< +0.255\text{ V}$. Pb(s) , Sn(s) , $\text{H}_2\text{(g)}$ will do the job.

27. Table D-4 contains the following data: $\text{Cr}^{3+}/\text{Cr}^{2+}$ reduction potential = -0.424 V , $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ reduction potential = 1.33 V and Cr^{2+}/Cr reduction potential = -0.90 V . The two unknown potentials are $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{2+}$, $E^\circ = 0.892\text{ V}$ and Cr^{3+}/Cr , $E^\circ = -0.74\text{ V}$.



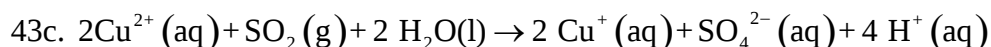
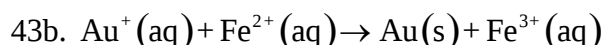
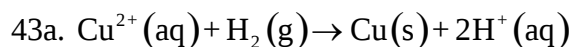
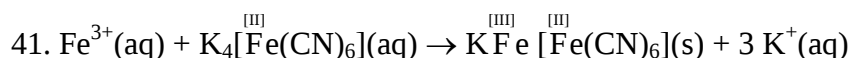
33a. 0.74 M

33b. $2.6 \times 10^{-5}\text{ M}$

35. 1.10 g Cr

37. Dichromate ion is the prevalent species in acidic solution. Oxoanions are better oxidizing agents in acidic solution because increasing the concentration of hydrogen ion favors formation of product. The half-equation is: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$. Notice also that CrO_4^{2-} is smaller than is $\text{Cr}_2\text{O}_7^{2-}$, giving it a higher lattice energy in its compounds, which makes these compounds harder to dissolve.

39. $E = 0.24\text{ V}$. Spontaneous under these conditions.



45a. No

45b. Yes

47. 0.912 V

49a. 0.02

49b. 0.02 atm

51. For ZnO , $\lambda = 413\text{ nm}$ (violet light). For CdS , $\lambda = 479\text{ nm}$ (blue light). The blue light absorbed by CdS is subtracted from the white light incident on the surface of the solid. The remaining reflected light is yellow in this case. When the violet light is subtracted from the white light incident on the ZnO surface, the reflected light appears white.

Advanced and Integrative Exercises

53. First, Ag^+ , the oxidation product, forms a very insoluble chloride, AgCl , which probably adheres to the surface of the metal and prevents further reaction. AuCl_3 is not noted as being an insoluble chloride. Second, gold(III) forms a very stable complex ion with chloride ion, $[\text{AuCl}_4]^-$. This complex ion is much more stable than the corresponding dichloroargentate ion, $[\text{AgCl}_2]^-$.

57a. $\text{Mo}(\text{CO})_6$

57b. $\text{Os}(\text{CO})_5$

57c. $\text{Re}(\text{CO})_5^-$

57d. The trigonal bipyramidal shape of nickel and iron carbonyls does not fit well in crystalline lattices, either because of its symmetry or repulsions with its neighbors and, consequently, these five-coordinate carbonyls are liquids at room temperature. Compare this to octahedral complexes ($\text{Cr}(\text{CO})_6$ and others), which are solids because they fit well into these lattices.

57e. This compound would be an ionic, salt-like material consisting of Na^+ and $\text{V}(\text{CO})_6^-$ ions.

61a. Dissolution: $\text{AgO}(\text{s}) + 2 \text{H}^+(\text{aq}) \longrightarrow \text{Ag}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Oxidation: $2 \text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^-$

Reduction: $\text{Ag}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}^+(\text{aq})$

61b. $E^\circ_{\text{cell}} = +0.75 \text{ V}$. Spontaneous.

64. 82.3%

65a. More of the 0.1000 M MnO_4^- solution would be required.

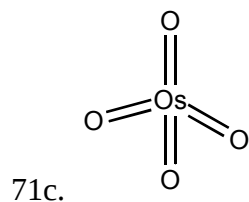
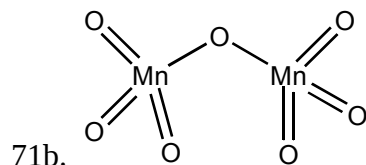
65b. 29.40 mL

67. % Mn = 3.286%, % Cr = 28.2%.

68a. $\text{NiC}_8\text{H}_{14}\text{O}_4\text{N}_4$

68b. 3.52%

71a. $\text{Hg} \text{---} \text{Hg}$



73. The empirical formula is NiTi. The % Ti by mass is 45%.

Feature Problems

74a. If $\Delta n_{\text{gas}} = 0$, then $\Delta S^\circ \sim 0$ and ΔG° is essentially independent of temperature ($\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$). If $\Delta n_{\text{gas}} > 0$, then $\Delta S^\circ > 0$ and ΔG° will become more negative with increasing temperature, hence the graph has a negative slope ($2 \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g})$). If $\Delta n_{\text{gas}} < 0$, then $\Delta S^\circ < 0$ and ΔG° will become more positive with increasing temperature, hence the graph has a positive slope ($2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$).

74b. the plot of ΔG° for the *net* reaction as a function of temperature will be a straight line with a slope of $-\left[\{\Delta S^\circ (\text{Rxn b})\} - \{\Delta S^\circ (\text{Rxn c})\}\right]$ (in kJ/K) and a y-intercept of $\left[\{\Delta H^\circ (\text{Rxn b})\} - \{\Delta H^\circ (\text{Rxn c})\}\right]$ (in kJ). the plot of ΔG° vs. T for the reaction will follow the equation $y = -0.176x + 172.5$. $P_{\text{CO}} = 5.7 \text{ atm}$.

Self-Assessment Exercises

79a. Impure iron (95% Fe).

79b. Iron-manganese alloy.

79c. $\text{Fe}(\text{CrO}_2)_2$

79d. An alloy of Zn and Cu with small amounts of Sn, Pb, and Fe.

79e. Mixture of $\text{HCl}(\text{aq})$ and $\text{HNO}_3(\text{aq})$.

79f. Impure $\text{Cu}(\text{s})$ containing $\text{SO}_2(\text{g})$.

79g. Iron alloy with varying quantities of metals such as Cr, Mn, and Ni, and a small and carefully controlled percentage of carbon.

80. The answers are (c), (f), and (g).

81. The answer is (b).

82. The answer is (d).

83. The answer is (a).

84. The answer is (d).

85. The answers are (c) and (e).

86a. $\text{CrO}_3(\text{s})$

86b. potassium manganate

86c. chromium carbonyl

86d. BaCr_2O_7

86e. lanthanum(III) sulfate nonahydrate

86f. $\text{Au}(\text{CN})_3 \cdot 3\text{H}_2\text{O}$

87a. $2\text{Fe}_2\text{S}_3(\text{s}) + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Fe}(\text{OH})_3(\text{s}) + 6\text{S}(\text{s})$

87b. $2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{S}_2\text{O}_8^{2-}(\text{aq}) \rightarrow 2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) + 10\text{SO}_4^{2-}(\text{aq})$

87c. $4\text{Ag}(\text{s}) + 8\text{CN}^-(\text{aq}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4[\text{Ag}(\text{CN})_2]^-(\text{aq}) + 4\text{OH}^-(\text{aq})$

88. Atoms of Zn, Cd and Hg have configurations of $4s^2 3d^{10}$, $5s^2 4d^{10}$, and $6s^2 4f^{14} 5d^{10}$, respectively. One the ns^2 electrons participate in bonding, and in this regard Zn, Cd, and Hg resemble the group 2 elements.

89. HNO_3 is the oxidizing agent for oxidizing the metal to Au^{3+} but Au^{3+} must be stabilized in solution. In aqua regia, Cl^- ions combine with Au^{3+} to form $[\text{AuCl}_4]^-$, which is stable in solution.

90. The Fe^{3+} ion forms a complex ion, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, in aqueous solution. The complex behaves as a weak monoprotic acid in solution.

Chapter 24 Answers

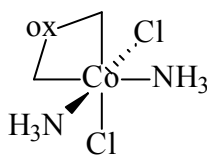
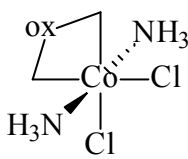
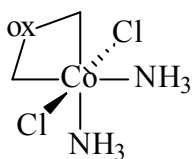
Practice Examples

1a. C.N. = 5, O.S. = +2.

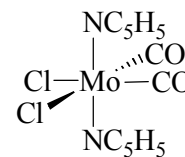
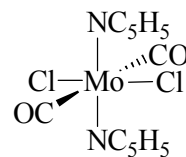
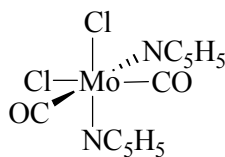
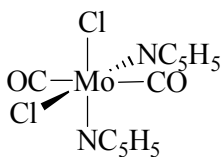
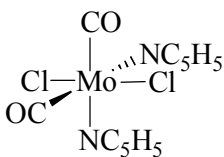
1b. $[\text{Fe}(\text{CN})_6]^{3-}$

2a. $\text{K}_2[\text{PtCl}_6]$

2b. pentaamminethiocyanato-S-cobalt(III) chloride



3a.



3b.

4a. Three

4b. There are three unpaired electrons in each case.

5a. $[\text{Co}(\text{CN})_4]^{2-}$ must be tetrahedral (3 unpaired electrons) and not octahedral (1 unpaired electron) because the magnetic behavior of a tetrahedral arrangement would agree with the experimental observations (3 unpaired electrons).

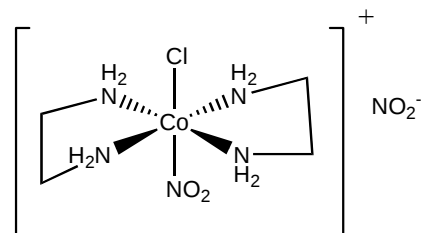
5b. The complex ion must be paramagnetic to the extent of one unpaired electron, regardless of the geometry the ligands adopt around the central metal ion.

6a. We are certain that $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is octahedral with a moderate field ligand. Tetrahedral $[\text{CoCl}_4]^{2-}$ has a weak field ligand. The relative values of ligand field splitting for the same ligand are $\Delta_t = 0.44 \Delta_o$. Thus, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ absorbs light of higher energy, blue or green light, leaving a light pink as the complementary color we observe. $[\text{CoCl}_4]^{2-}$ absorbs lower energy red light, leaving blue light to pass through and be seen.

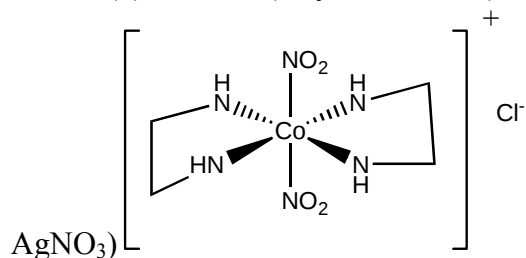
6b. $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ should appear yellow. $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ should be green.

Integrative Example

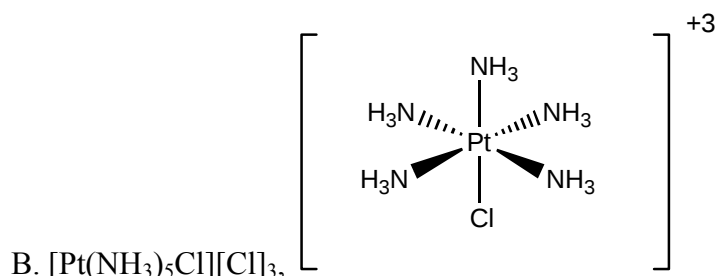
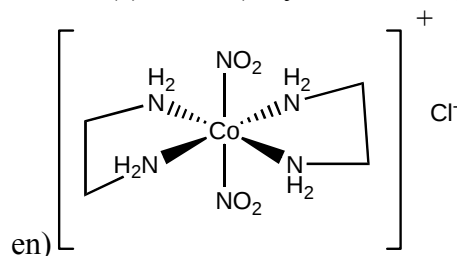
A. (a) *trans*-chlorobis(ethylenediamine)nitrito-*N*-cobalt(III) nitrite (no reaction with AgNO₃)



(b) *trans*-bis(ethylenediamine)dinitrito-*N*-cobalt(III) chloride (reacts with



(c) *cis*-bis(ethylenediamine)dinitrito-*N*-cobalt(III) chloride (reacts with AgNO₃ and



B. [Pt(NH₃)₅Cl][Cl]₃,

Exercises

1a. [CrCl₄(NH₃)₂]⁻, diamminetetrachlorochromate(III) ion.

1b. [Fe(CN)₆]³⁻, hexacyanoferrate(III) ion.

1c. [Cr(en)₃]₂[Ni(CN)₄]₃, tris(ethylenediamine)chromium(III) tetracyanonickelate(II) ion.

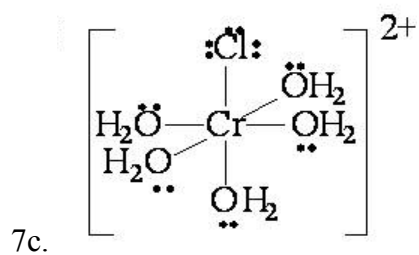
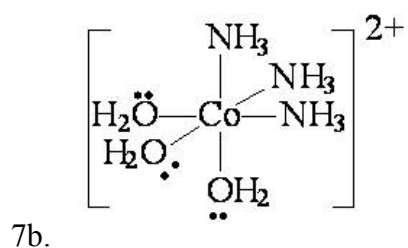
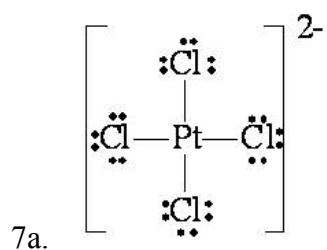
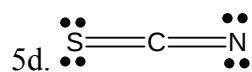
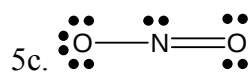
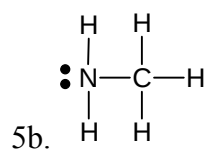
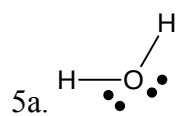
3a. amminetetraaquahydroxocobalt(III) ion

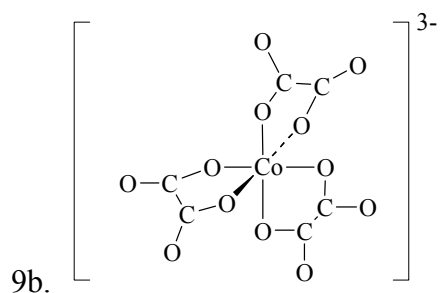
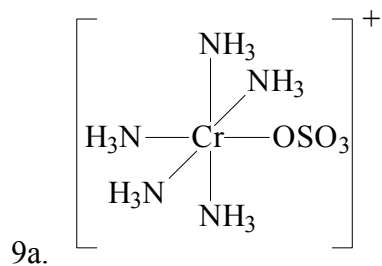
3b. triamminetrinitrito-*O*-cobalt(III)

3c. tetraaquaplatinum(II) hexachloroplatinate(IV)

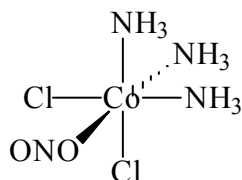
3d. diaquadioxalatoferrate(III) ion

3e. silver(I) tetraiodomercurate(II)

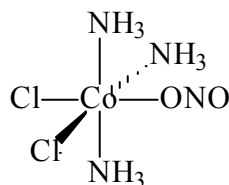




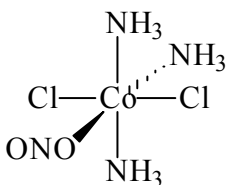
fac-triamminedichloronitro-O-cobalt(III)



mer-triammine-*cis*-dichloronitro-O-cobalt(III)



mer-triammine-*trans*-dichloronitro-O-cobalt(III)



9c.

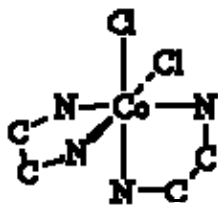
11a. Tetrahedral structures do not display *cis-trans* isomerism.

11b. Square planar structures can show *cis-trans* isomerism.

11c. Linear structures do not display *cis-trans* isomerism.

13a. Three

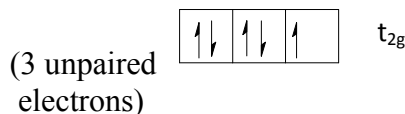
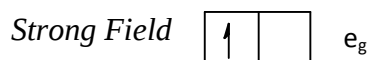
13b. Yes



15. The *cis*-dichlorobis(ethylenediamine)cobalt(III) ion is optically active. The *trans*-isomer is not optically active.

17. In crystal field theory, the five *d* orbitals of a central transition metal ion are split into two (or more) groups of different energies. The energy spacing between these groups often corresponds to the energy of a photon of visible light. Thus, the transition-metal complex will absorb light with energy corresponding to this spacing. If white light is incident on the complex ion, the light remaining after absorption will be missing some of its components. Thus, light of certain wavelengths (corresponding to the energies absorbed) will no longer be present in the formerly white light. The resulting light is colored.

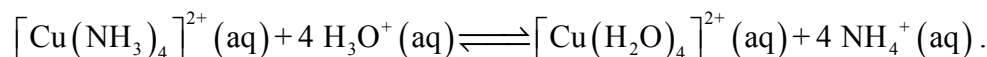
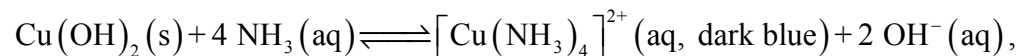
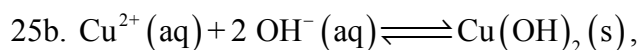
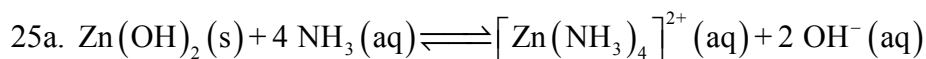
19.



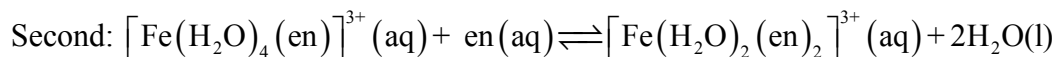
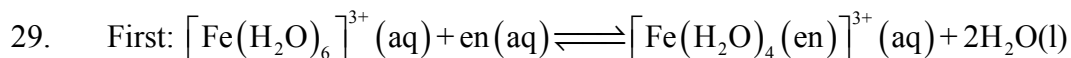
21a. The Mo complex is paramagnetic. The Co complex is diamagnetic.

21b. Three

23. The octahedral and tetrahedral configurations have the same number of unpaired electrons. The magnetic behavior cannot be used to determine whether the ammine complex of nickel(II) is octahedral or tetrahedral.



27. $[\text{Co}(\text{en})_3]^{3+}$ should have the largest overall K_f value.



Third: $[\text{Fe}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}(\text{aq}) + \text{en}(\text{aq}) \rightleftharpoons [\text{Fe}(\text{en})_3]^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ $K_f = 5.0 \times 10^9 = \beta_3$

31a. Aluminum(III) forms a stable (and soluble) hydroxo complex but not a stable ammine complex.

31b. Although zinc(II) forms a soluble stable ammine complex ion, its formation constant is not sufficiently large to dissolve highly insoluble ZnS. However, it is sufficiently large to dissolve the moderately insoluble ZnCO_3 .

31c. Chloride ion forms a stable complex ion with silver(I) ion, that dissolves the $\text{AgCl}(\text{s})$ that formed when $[\text{Cl}^-]$ is low.

33. $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$

35a. $K_{\text{overall}} = K_{\text{sp}} \times K_f = 8.5$. With a reasonably high $[\text{S}_2\text{O}_3^{2-}]$, this reaction will go essentially to completion.

35b. $\text{NH}_3(\text{aq})$ cannot be used in the fixing of photographic film because of the relatively small value of K_f for $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$, $K_f = 1.6 \times 10^7$. This would produce a value of $K = 8.0 \times 10^{-6}$ which is nowhere large enough to drive the reaction to completion.

37. To make the *cis* isomer, ligands that show a strong tendency for directing incoming ligands to positions that are *trans* to themselves must be used. Γ^- has a stronger tendency than does Cl^- or NH_3 for directing incoming ligands to the *trans* positions, and so it is beneficial to convert $\text{K}_2[\text{PtCl}_4]$ to $\text{K}_2[\text{PtI}_4]$ before replacing ligands around Pt with NH_3 molecules.

Integrative and Advanced Exercises

39a. tetraamminecopper(II) ion, $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

39b. tetraamminedichlorocobalt(III) chloride, $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$.

39c. hexachloroplatinate(IV) ion, $[\text{PtCl}_6]^{2-}$.

39d. sodium tetrachlorocuprate(II), $\text{Na}_2[\text{CuCl}_4]$,

39e. potassium pentachloroantimonate(III), $\text{K}_2[\text{SbCl}_5]$.

40. $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, tetraammineplatinum(II) tetrachloroplatinate(II).

45. The successive acid ionizations of a complex ion such as $[\text{Fe}(\text{OH})_6]^{3+}$ are more nearly equal in magnitude than those of an uncharged polyprotic acid such as H_3PO_4 principally because the complex ion has a positive charge. The second proton is leaving a species which has one fewer positive charge but which is nonetheless positively charged. Since positive charges repel each other, successive ionizations should not show a great decrease in the magnitude of their ionization constants.

47a. 2.02

47b. 9.0×10^{-4} M

47c. $[\text{H}_3\text{O}^+] = 90$. M. An impossibly high concentration of H_3O^+ would be required.

51. Total $[\text{Cl}^-] = 0.52$ M.

52a. $4 \text{Co}^{3+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \longrightarrow 4 \text{Co}^{2+}(\text{aq}) + 4 \text{H}^+(\text{aq}) + \text{O}_2(\text{g})$, $E^\circ_{\text{cell}} = +0.59$ V.

52b. $[\text{Co}^{3+}] = 2.2 \times 10^{-28}$ M.

52c. $E = -0.142$ V. The negative cell potential indicates that the reaction indeed does not occur.

54. $E = +0.99$ V

57. The Cr^{3+} ion would have 3 unpaired electrons, each residing in a $3d$ orbital and would be sp^3d^2 hybridized. The hybrid orbitals would be hybrids of $4s$, $4p$, and $3d$ (or $4d$) orbitals. Each Cr-NH_3 coordinate covalent bond is a σ bond formed when a lone pair in an sp^3 orbital on N is directed toward an empty sp^3d^2 orbital on Cr^{3+} . The number of unpaired electrons predicted by valence bond theory would be the same as the number of unpaired electrons predicted by crystal field theory.

62. The coordination compound is face-centered cubic, K^+ occupies tetrahedral holes, while PtCl_6^{2-} occupies octahedral holes.

63. In order from 0 NH_3 ligands to 6 NH_3 ligands: $\text{K}_2[\text{PtCl}_6]$, $\text{K}[\text{PtCl}_5(\text{NH}_3)]$, $\text{PtCl}_4(\text{NH}_3)_2$, $[\text{PtCl}_3(\text{NH}_3)_3]\text{Cl}$, $[\text{PtCl}_2(\text{NH}_3)_4]\text{Cl}_2$, $[\text{PtCl}(\text{NH}_3)_5]\text{Cl}_3$, $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$.

Feature Problems

64a. A trigonal prismatic structure predicts three geometric isomers for $[\text{CoCl}_2(\text{NH}_3)_4]^+$, which is one more than the actual number of geometric isomers found for this complex ion.

64b. Barring any unusual stretching of the ethylenediamine ligand, a trigonal prismatic structure cannot account for the optical isomerism that was observed for $[\text{Co}(\text{en})_3]^{3+}$.

Self-Assessment Exercises

70. The answer is (d).

71. The answer is (e).

72. The answer is (b).

73. The answer is (a).

74. The answer is (d).

75. The answer is (c).

76. The answer is (b).

77a. pentaamminebromocobalt(III)sulfate, no isomerism.

77b. hexaamminechromium(III)hexacyanocobaltate(III), no isomerism.

77c. sodiumhexanitrito-N-cobaltate(III), no isomerism

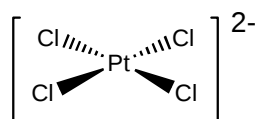
77d. tris(ethylenediamine)cobalt(III)chloride, two optical isomers.

78a. $[\text{Ag}(\text{CN})_2]^-$

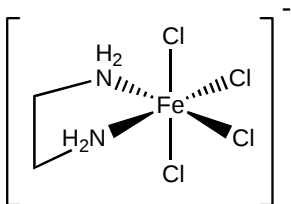
78b. $[\text{Pt}(\text{NO}_2)(\text{NH}_3)_3]^+$

78c. $[\text{CoCl}(\text{en})_2(\text{H}_2\text{O})]^{2+}$

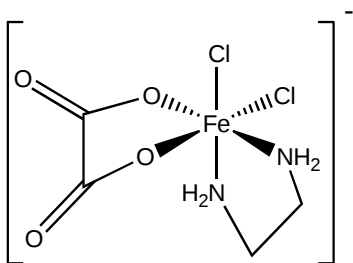
78d. $\text{K}_4[\text{Cr}(\text{CN})_6]$



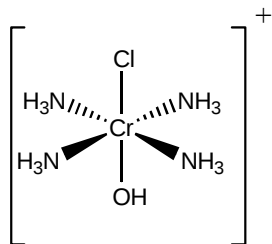
79a.



79b.



79c.

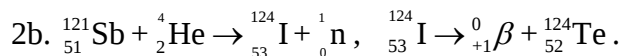
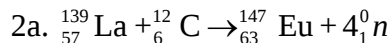
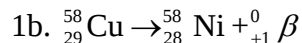
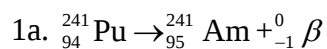


79d.

- 80a. One
- 80b. Two
- 80c. Two
- 80d. Two
- 81a. Coordination isomerism
- 81b. Linkage isomerism
- 81c. No isomerism
- 81d. Geometric isomerism
- 81e. Geometric isomerism
- 82a. Geometric isomerism (*cis* and *trans*) and optical isomerism in the *cis* isomer.
- 82b. Geometric isomerism (*cis* and *trans*), optical isomerism in the *cis* isomer, and linkage isomerism in the thiocyanate ligand.
- 82c. No isomers.
- 82d. No isomers.
- 82e. Two geometric isomers, one with the tridentate ligand occupying meridional positions and the other with the tridentate ligand occupying facial positions.
83. $[\text{Co}(\text{en})_3]^{3+}(\text{aq})$ is yellow and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ is blue.

Chapter 25 Answers

Practice Examples



3a. (a) $9.98 \times 10^{-7} \text{ s}^{-1}$; (b) 9.40×10^{12} disintegrations / second; (c) 2.36×10^{18} atoms; (d) 2.36×10^{12} dis / s.

3b. 75.8 d

4a. $4.7 \times 10^3 \text{ y}$

4b. 13 dis / min (per gram of C)

5a. 2.544 MeV

5b. 0.006001 u

6a. (a) Stable; (b) Radioactive; (c) Radioactive.

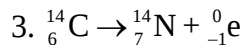
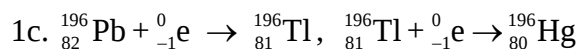
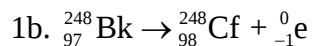
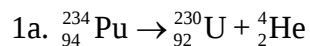
6b. Positron emission by ${}^{17}\text{F}$ to produce ${}^{17}\text{O}$ and β^- emission by ${}^{22}\text{F}$ to produce ${}^{22}\text{Ne}$.

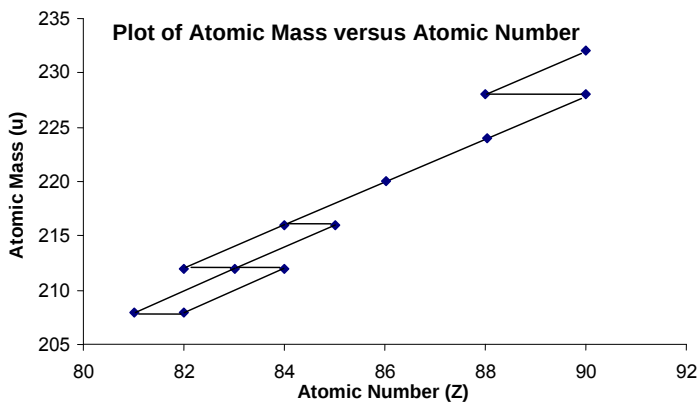
Integrative Example

A. 0.14

B. (a) Yes; (b) 4.67×10^{40} ; (c) Yes; (d) Possibly yes.

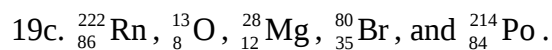
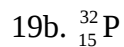
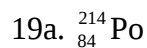
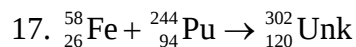
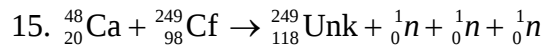
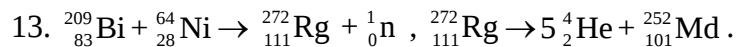
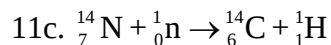
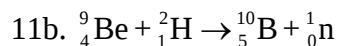
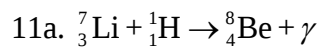
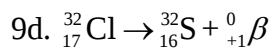
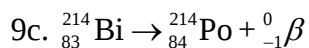
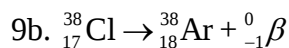
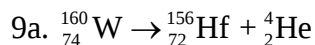
Exercises





5.

7. In Figure 25–2, only the following mass numbers are represented: 206, 210, 214, 218, 222, 226, 230, 234, and 238. The mass numbers are separated from each other by 4 units. The first of them, 206, equals $(4 \times 51) + 2$, that is $4n + 2$, where $n = 51$.



25. 142 days

27. The object is a bit more than 3000 years old, and thus is probably not from the pyramid era, which occurred about 3000 B.C.

29. 0.12

31. 3.03×10^9 y

33a. 5.42×10^{-9} J

33b. 3727 MeV

35. 7.805 MeV/nucleon

37. 4.06 MeV

39. 7.26×10^3 neutrons

41a. ^{20}Ne

41b. ^{18}O

41c. ^7Li

43a. ^{29}P should decay by β^+ emission. ^{33}P should decay by β^- emission.

43b. ^{120}I should decay by β^+ emission. ^{134}I should decay by β^- emission.

45. A “doubly magic” nuclide is one in which the atomic number is a magic number (2, 8, 20, 28, 50, 82, 114) and the number of neutrons also is a magic number (2, 8, 20, 28, 50, 82, 126, 184). An example is ^{16}O .

47. 1.37 mg

49. The rem takes into account the quantity of biological damage done by a given dosage of radiation. The rad is the dosage that places 0.010 J of energy into each kilogram of irradiated matter. For living tissue, the rem provides a good idea of how much tissue damage a certain kind and quantity of radiation damage will do. But for nonliving materials, the rad is usually preferred.

51. One reason why ^{90}Sr is hazardous is because strontium is in the same family of the periodic table as calcium, and hence often reacts in a similar fashion to calcium. The most likely place for calcium to be incorporated into the body is in bones, where it resides for a long time. Strontium is expected to behave in a similar fashion. Thus, it will be retained in the body for a long time.

53. Mix a small amount of tritium with the H_2 (g) and detect where the radioactivity appears with a Geiger counter.

55. The recovered sample will be radioactive. When NaCl(s) and $\text{NaNO}_3\text{(s)}$ are dissolved in solution, the ions are free to move throughout the solution. A given anion does not remain associated with a particular cation. Thus, all the anions and cations are shuffled and some of the radioactive ^{24}Na will end up in the crystallized NaNO_3 .

59. 2.9×10^3 metric tons

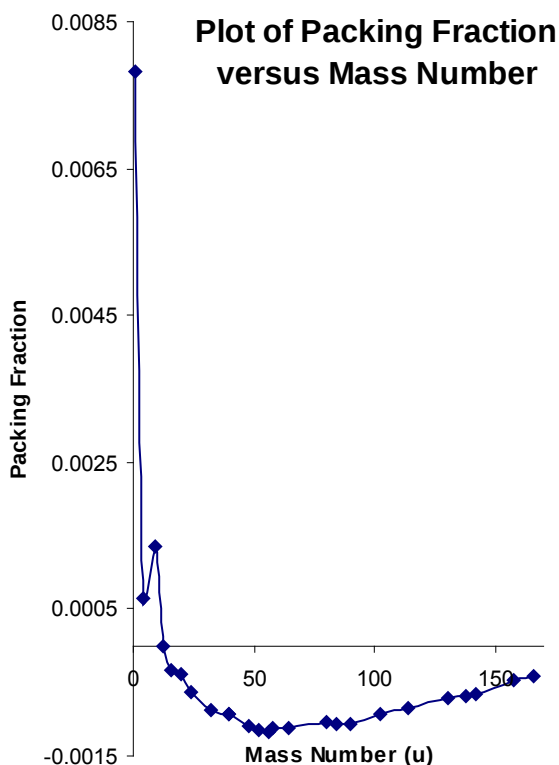
62. $7.0 \times 10^{-6} \text{ g } ^{90}\text{Sr}$

63. 29 y

67. $2.0 \times 10^2 \text{ Ci}$

68. $1.2 \times 10^7 \text{ kJ}$

Feature Problems



72. The graph and Fig. 25-6 are almost exactly the inverse of one another, with the maxima of one being the minima of the other.

73a. The rate of decay depends on both the half-life and the number of radioactive atoms present. In the early stages of the decay chain, the larger number of radium-226, atoms multiplied by the very small decay constant is still larger than the product of the very small number of radon-222 atoms and its much larger decay constant. Only after some time has elapsed, does the rate of decay of radon-222 approach the rate at which it is formed from radium-226 and the amount of

radon-222 reaches a maximum. Beyond this point, the rate of decay of radon-222 exceeds its rate of formation.

$$73b. \frac{dD}{dt} = \lambda_p P - \lambda_d D = \lambda_p P_0 e^{-\lambda_p t} - \lambda_d D$$

73c. 1 year

74a. 87.5 u

74b. 267.44 ppm

74c. 2.95%

74d. 2.07×10^9 years

Self-Assessment Exercises

78. The answer is (c).

79. The answer is (b).

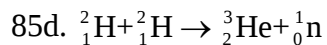
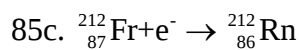
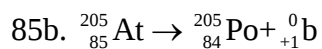
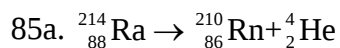
80. The answer is (d).

81. The answer is (c).

82. The answer is (c).

83. The answer is (d).

84. The answer is (d).



86. 76 days

87a. 174 days

87b. 287 days

87c. 375 days

88. The answer is (b).

89. The answer is (d).

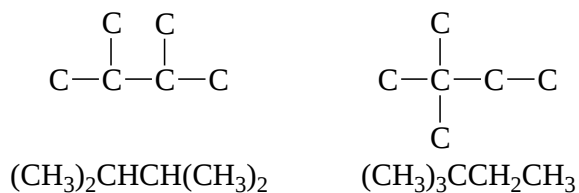
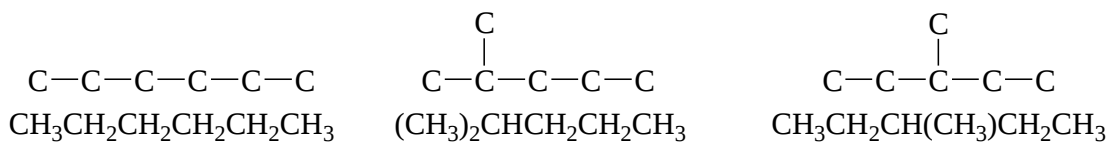
90. The answer is (c).

91. The answer is (a).

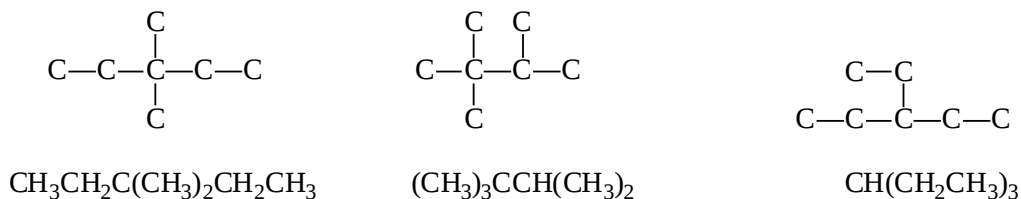
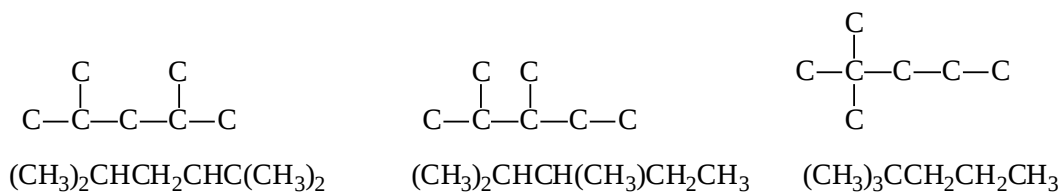
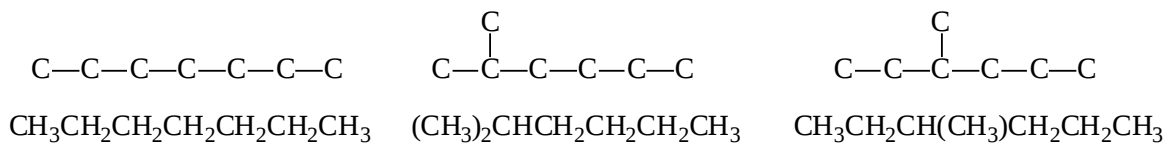
92. The answer is (b).

Chapter 26 Answers

Practice Examples



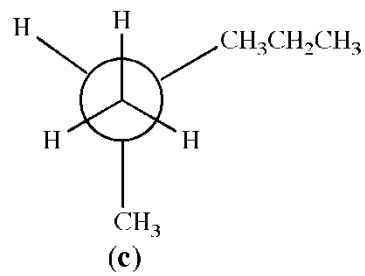
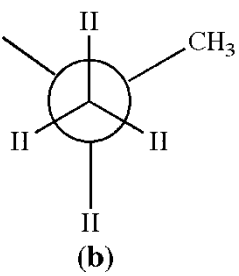
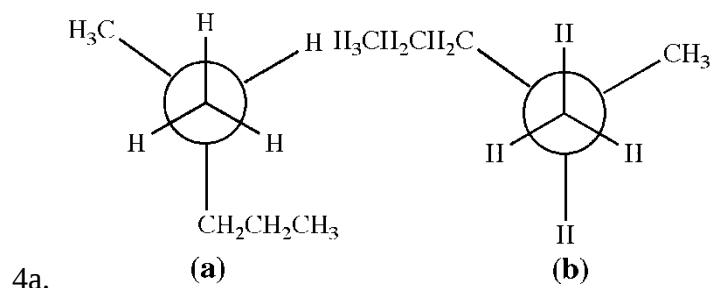
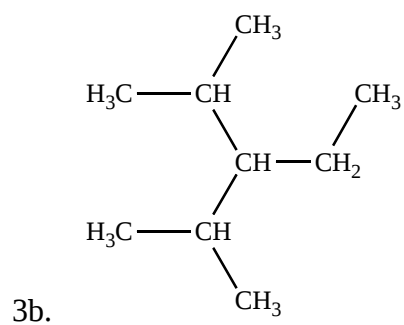
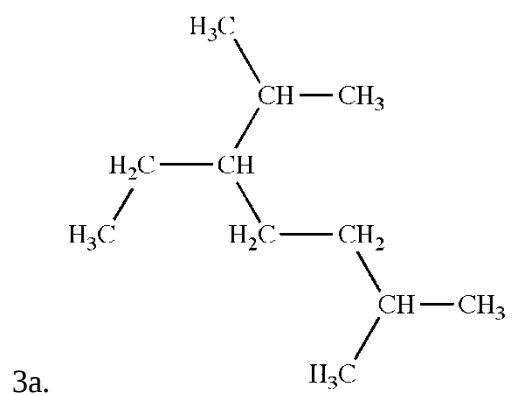
1a.



1b.

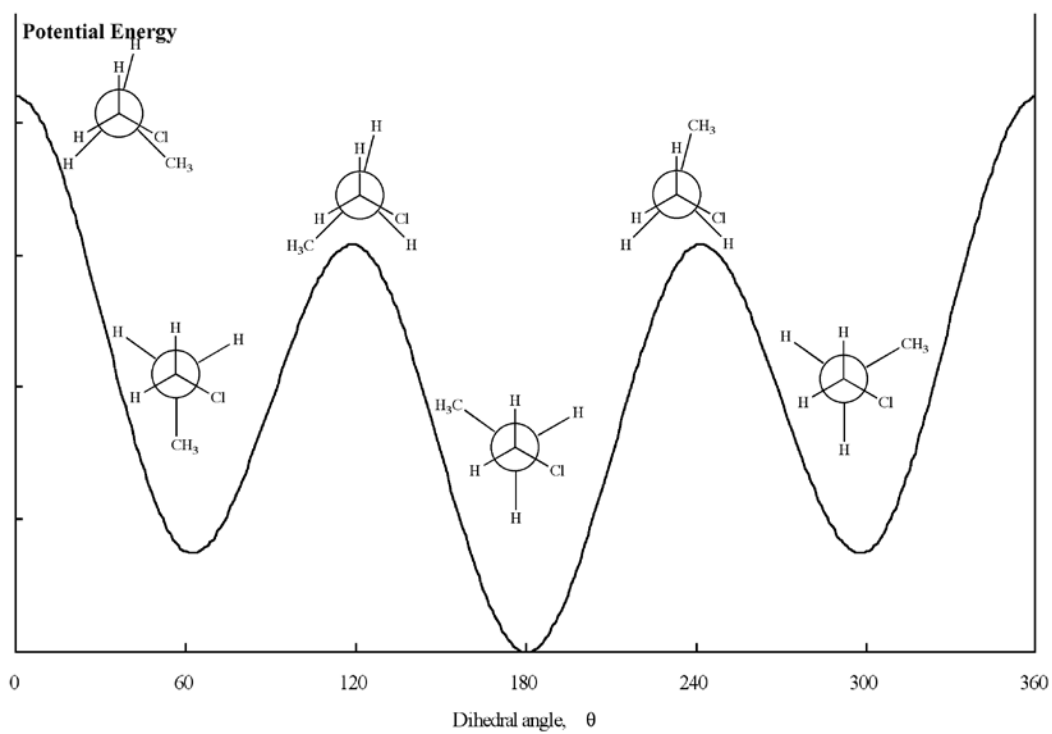
2a. 3,6,6-trimethyloctane

2b. 3,6-dimethyloctane

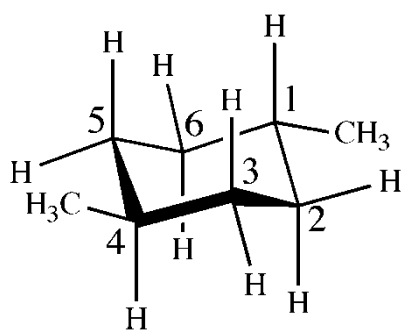


conformations have the same energy.

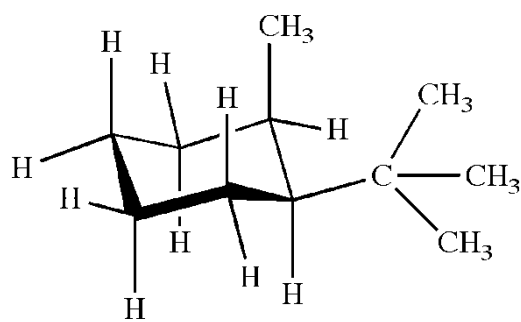
All



4b.



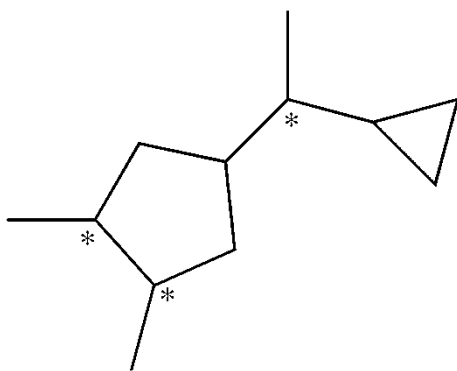
5a.



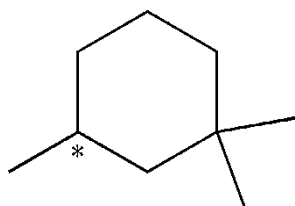
5b.

6a. (a) Achiral; (b) Chiral; (c) Chiral.

6b. (a) Achiral; (b) Chiral; (c) Chiral.



7a.

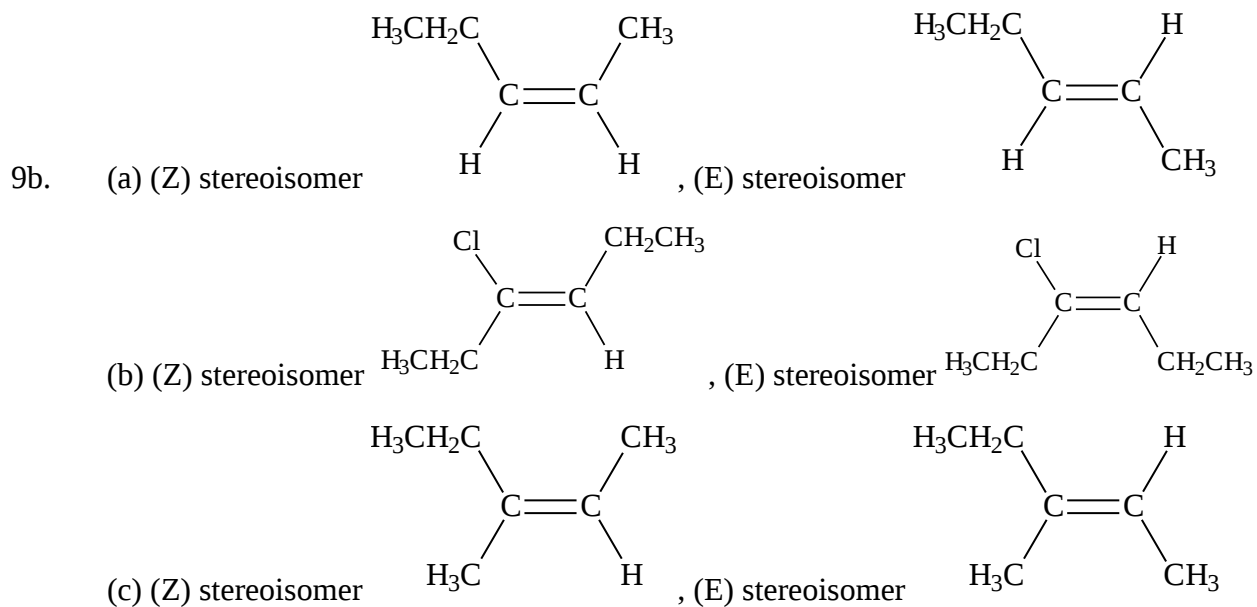


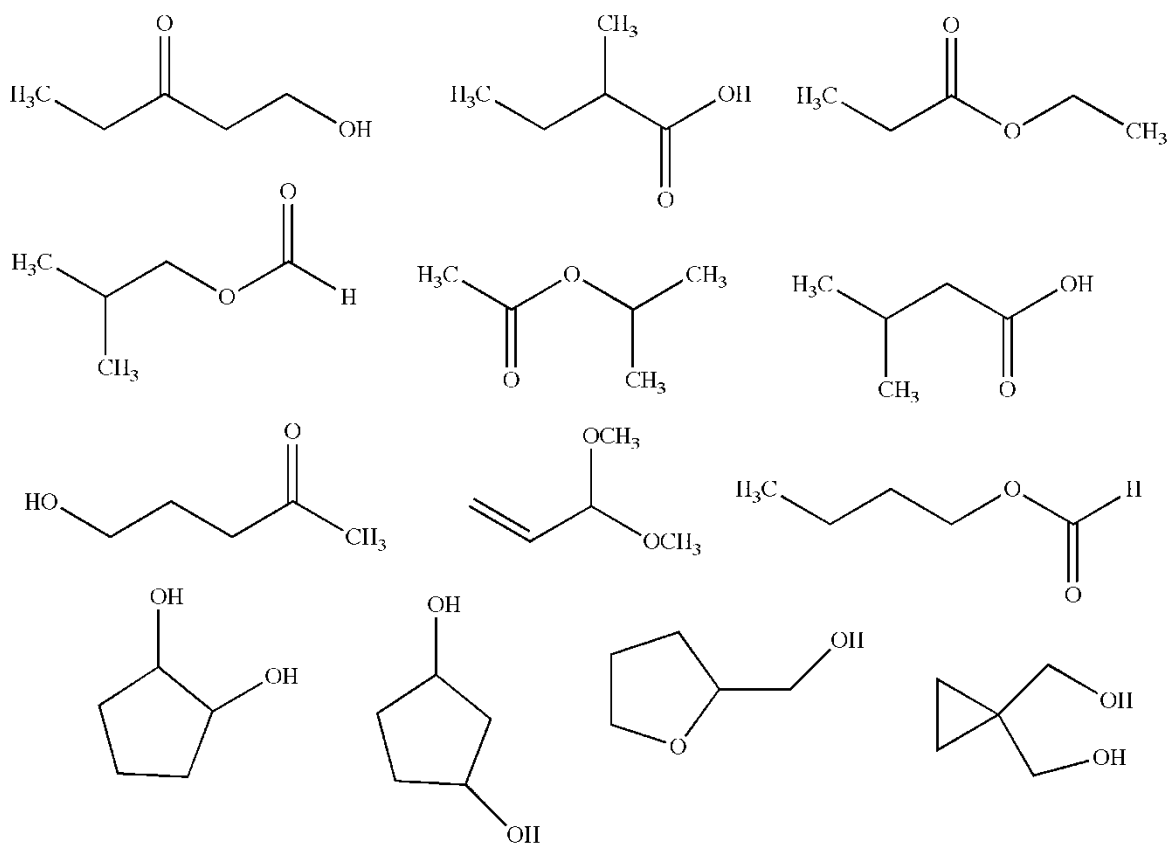
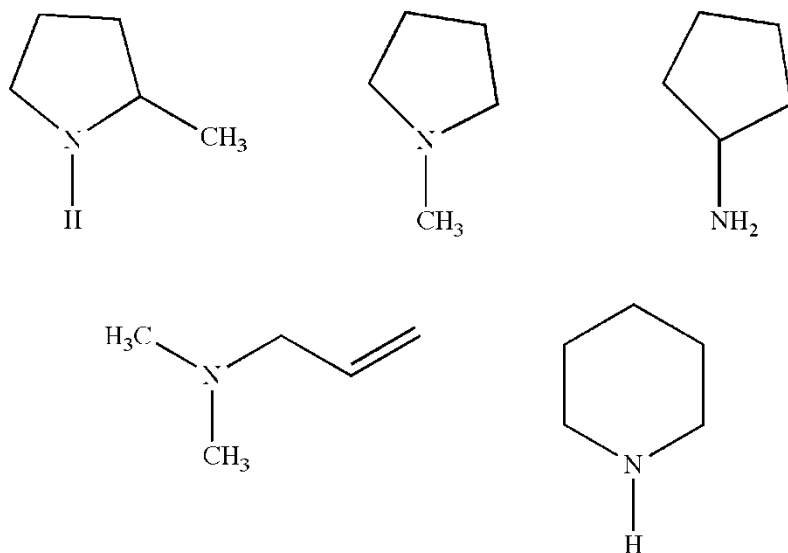
7b.

8a. (a) R configuration; (b) R configuration; (c) R configuration.

8b. (a) Enantiomers; (b) Enantiomers.

9a. (a) (E) stereoisomer; (b) (Z) stereoisomer; (c) (Z) stereoisomer.





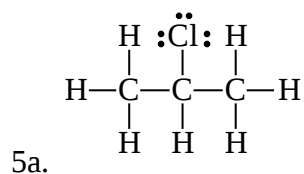
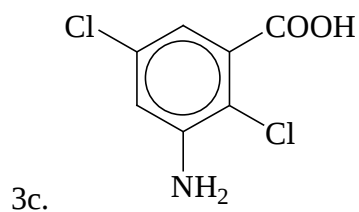
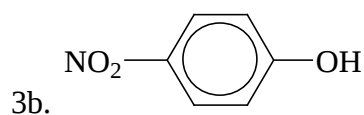
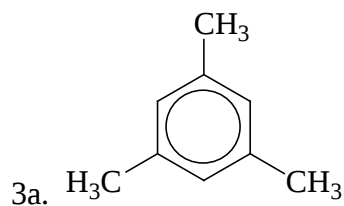
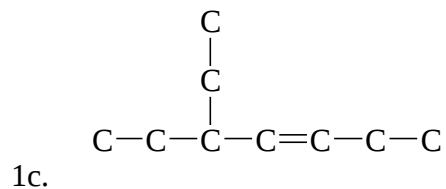
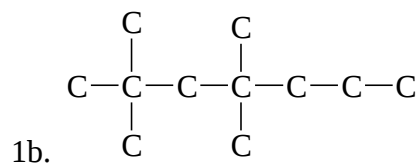
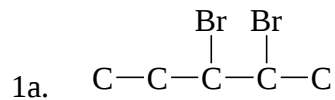
Integrative Example

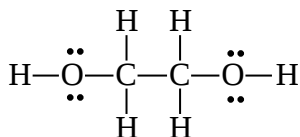
A. $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$ (Compound A), $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$ (Compound B), $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COO-CH}_3\text{-CH}_2$ (Compound C).

B. Compounds (a) and (b) are both ethers. Ethers are relatively unreactive and the ether linkage is stable in the presence of most oxidizing and reducing agents, as well as dilute acids and

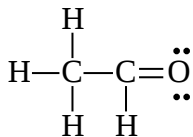
alkalis. Compound (c) is unsaturated secondary alcohol. It will decolorize a Br_2/CCl_4 solution. Compound (d), on the other hand is an aldehyde. On treatment with chromic acid it will be oxidized to carboxylic acid.

Exercises



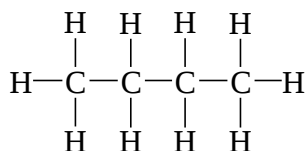


5b.

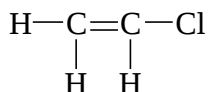


5c.

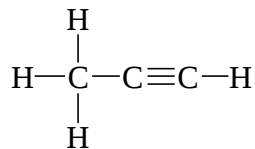
7a. Each carbon atom is sp^3 hybridized. All of the C–H bonds in the structure are sigma bonds, between the 1s orbital of H and the sp^3 orbital of C. The C–C bond is between sp^3 orbitals on each C atom.



7b. Both carbon atoms are sp^2 hybridized. All of the C–H bonds in the structure are sigma bonds between the 1s orbital of H and the sp^2 orbital of C. The C–Cl bond is between the sp^2 orbital on C and the 3p orbital on Cl. The C = C double bond is composed of a sigma bond between the sp^2 orbitals on each C atom and a pi bond between the $2p_z$ orbitals on the two C atoms.



7c. The left-most C atom is sp^3 hybridized, and the C–H bonds to that C atom are between the sp^3 orbitals on C and the 1s orbital on H. The other two C atoms are sp hybridized. The right-hand C–H bond is between the sp orbital on C and the 1s orbital on H. The C $\equiv$ C triple bond is composed of one sigma bond formed by overlap of sp orbitals, one from each C atom, and two pi bonds, each formed by the overlap of two $2p$ orbitals, one from each C atom (that is a $2p_y$ — $2p_y$ overlap and a $2p_z$ — $2p_z$ overlap).



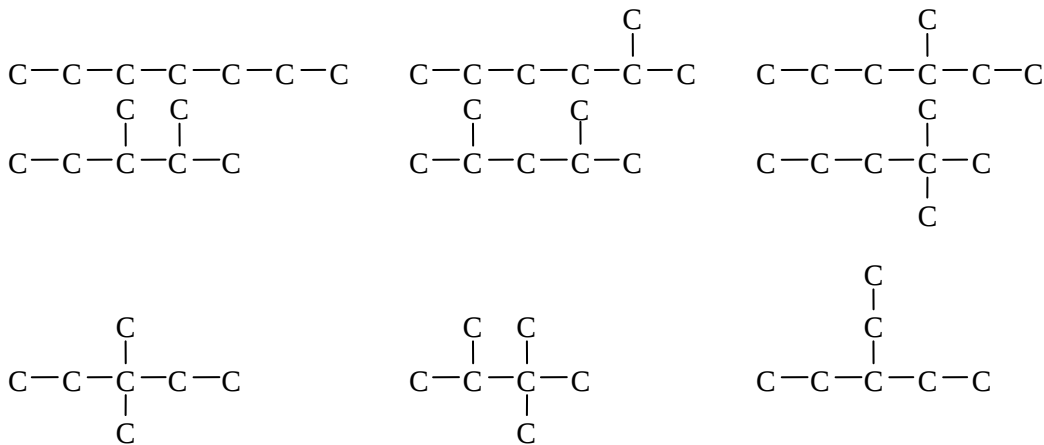
9a. Identical

9b. Constitutional isomers

9c. No relationship

9d. Constitutional isomers

9e. Stereoisomers



13a. Carbon 2 is chiral.

13b. There are no chiral carbon atoms.

13c. Carbon 2 is chiral.

15a. Carbon 2 is chiral.

15b. Carbon 2 is chiral.

15c. There are no chiral carbon atoms.

17a. Alkyl halide

17b. Aldehyde

17c. Ketone

17d. Phenol, hydroxyl group, and phenyl group.

19a. The hydroxyl group.

19b. An aldehyde has a carbonyl group with a hydrogen and a carbon group attached. In a ketone, the carbonyl group is attached to two carbons.

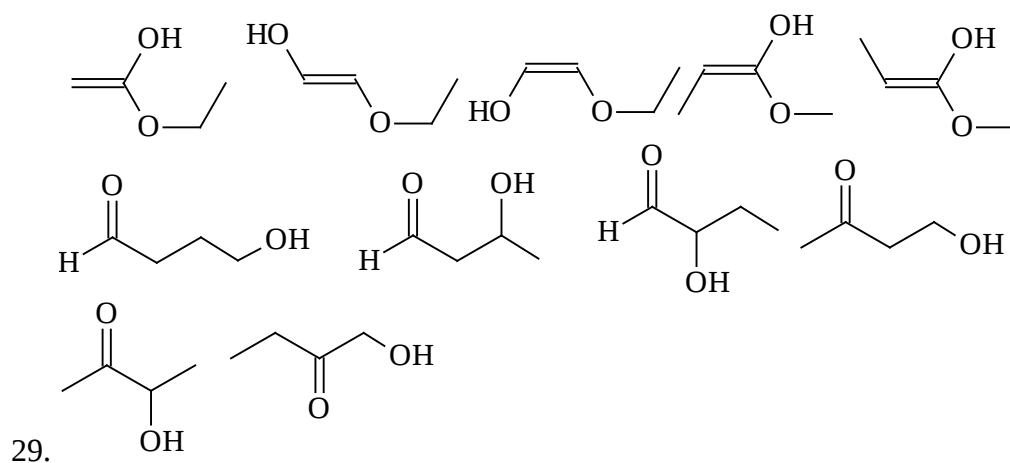
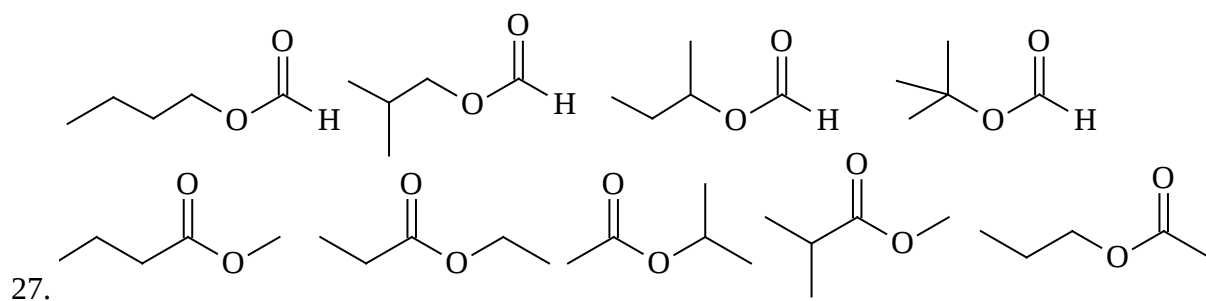
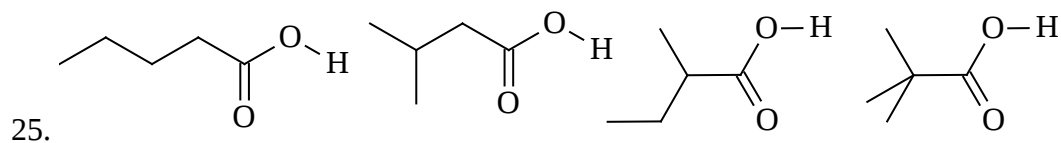
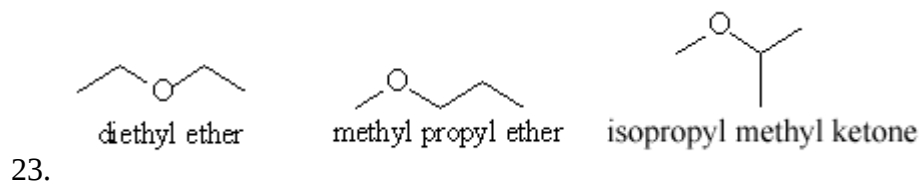
19c. The essential difference is the presence of the — OH group in acetic acid.

21a. Carboxylic acid, hydroxyl group and disubstituted aromatic ring.

21b. Ester group

21c. Ketone and carboxylic acid group.

21d. Aldehyde, hydroxyl group, and disubstituted aromatic ring.



31a. 3,5-dimethyloctane

31b. 2,2-dimethylpropane

31c. 3,3-dichloro-5-ethylheptane

33a. 2,2-dimethylbutane

33b. 2-methylpropene

33c. 1,2-dimethylcyclopropane

33d. 4-methyl-2-pentyne

33e. 3,4-dimethylhexane

33f. 3,4-dimethyl-2-propyl-1-pentene

35a. Insufficient

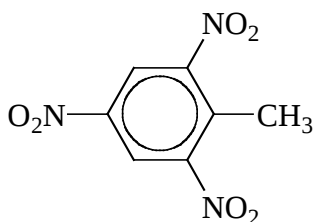
35b. Sufficient

35c. Insufficient

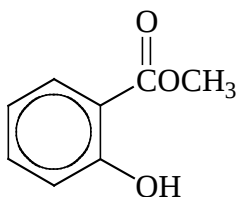
35d. Insufficient

35e. Sufficient

35f. Insufficient



37a.



37b.

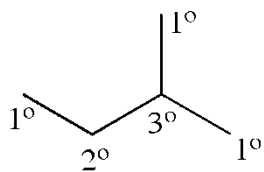
37c. $\text{HOOCCH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$

39a. *N,N*-diethylamine

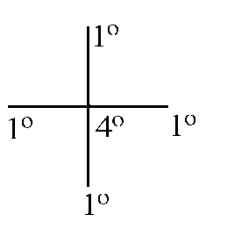
39b. *p*-nitroaniline

39c. *N*-cyclopentyl-*N*-ethylamine

39d. *N,N*-diethyl-*N*-methylamine

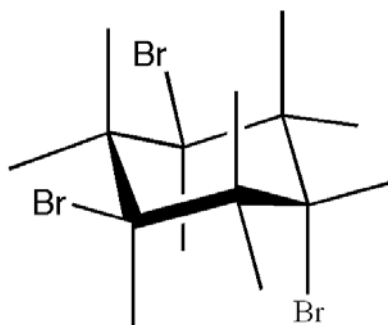


41a.

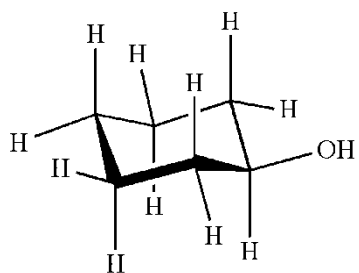


41b.

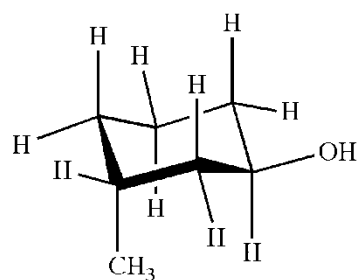
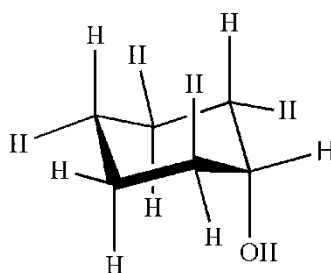
43. The Anti conformation is lowest in energy.



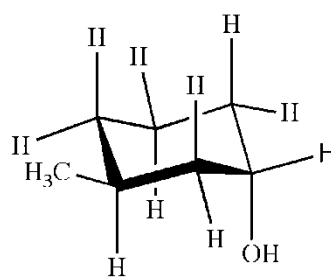
45.



47a.



47b.



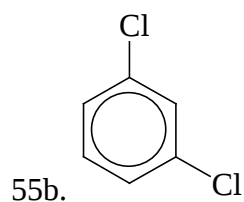
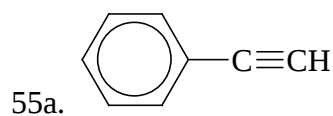
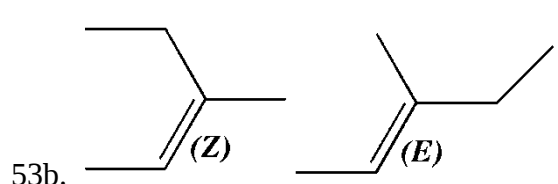
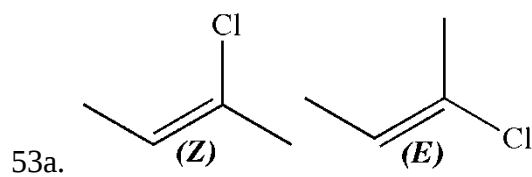
49. In the case of ethene there are only two carbon atoms between which there can be a double bond. In the case of propene, there can be a double bond only between the central carbon atom

and a terminal carbon atom. The case of butene is different since 1-butene is distinct from 2-butene.

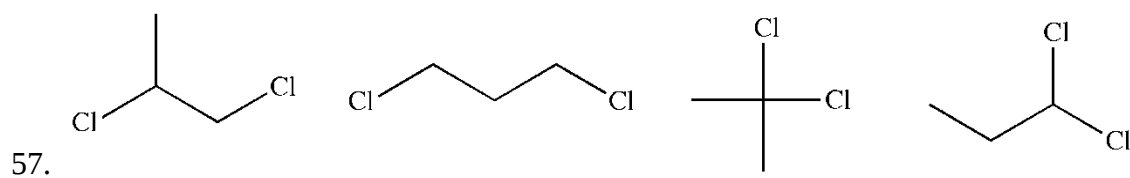
51a. (E) configuration

51b. (Z) configuration

51c. (E) configuration



55c. 1,3,5-trihydroxybenzene



59a. Identical

59b. Identical

59c. Isomers

59d. Enantiomers

59e. Identical

61a. (S)-3-bromo-2-methylpentane

61b. (S)-1,2-dibromopentane

61c. (R)-3-(bromomethyl)-1-chloropentan-3-ol

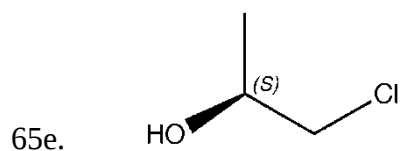
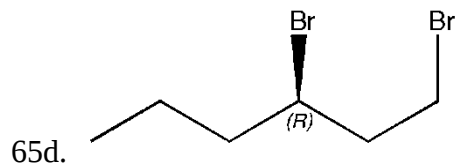
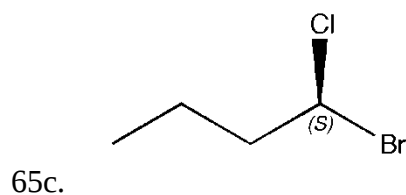
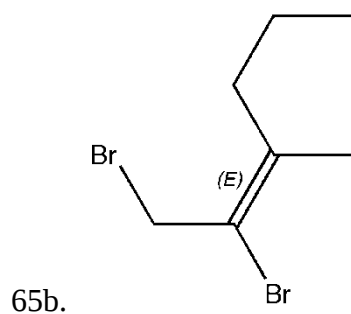
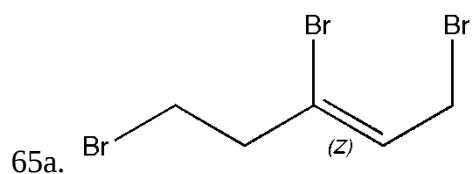
61d. (S)-1-bromopropan-2-ol

63a. (Z)-pent-2-ene

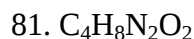
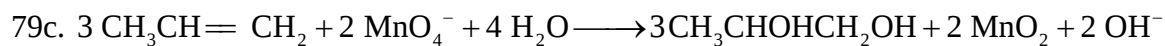
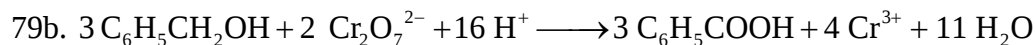
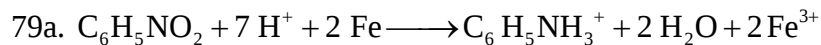
63b. (E)-1-chloro-2-methylbut-1-ene

63c. (E)-4-(chloromethyl)-3,7-dimethyloct-3-ene

63d. (Z)-5-bromo-3-(bromomethyl)-2-methylpent-2-enal



Integrative and Advanced Exercises



84. The unknown must be 1-butanol or butyraldehyde. The identity of the unknown can be established by treatment with a carboxylic acid.

89a. Ester, amine(tertiary), arene.

89b. $\text{C}_1 = \text{sp}^2$, $\text{C}_2 = \text{sp}^3$, $\text{C}_3 = \text{sp}^3$, $\text{C}_4 = \text{sp}^3$, $\text{N} = \text{sp}^3$.

89c. Carbons 2 and 4 are chiral.

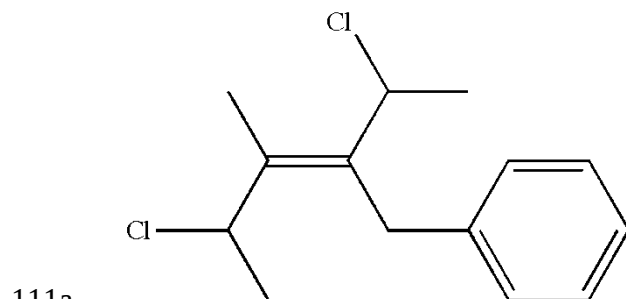
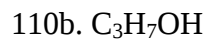
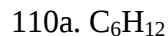
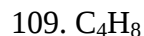
Self-Assessment Exercises

101. The correct answer is (c).

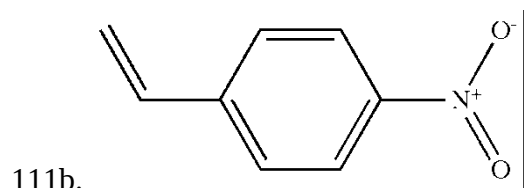
102. The correct answer is (b).

103. The correct answer is (e).

108. The correct answer is (c).

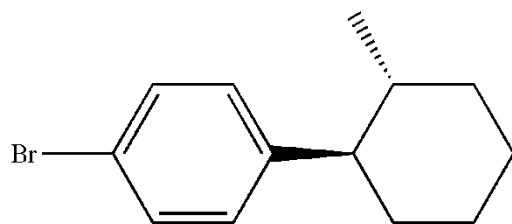


111a.



111b.

111c.

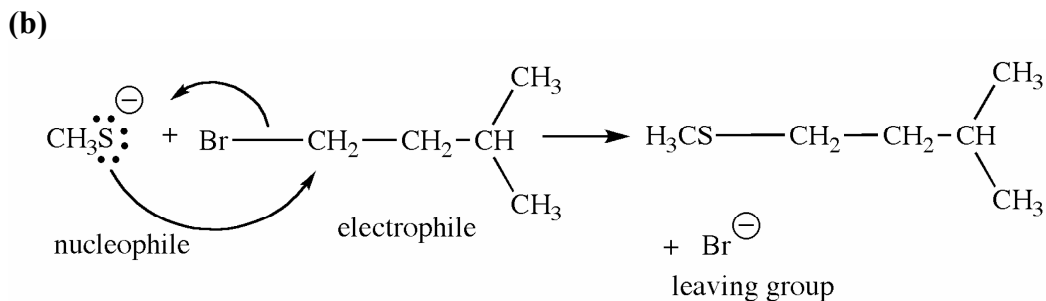
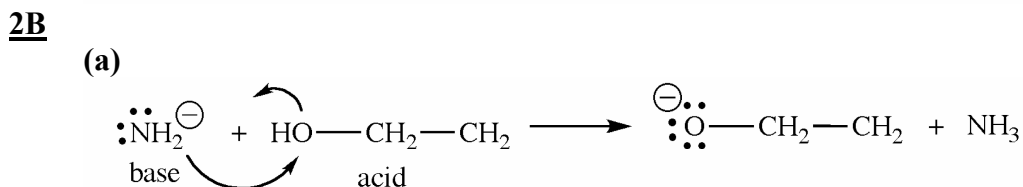
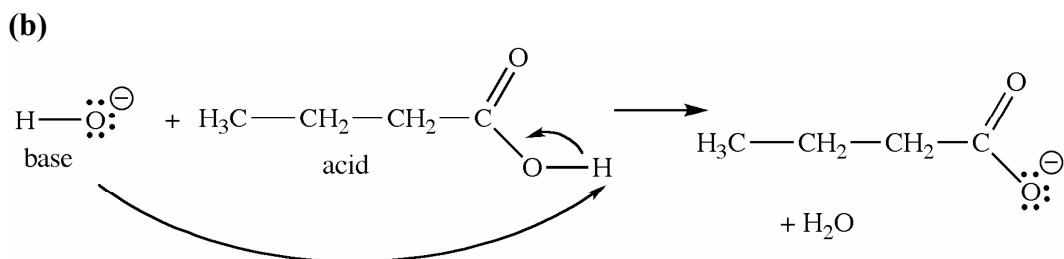
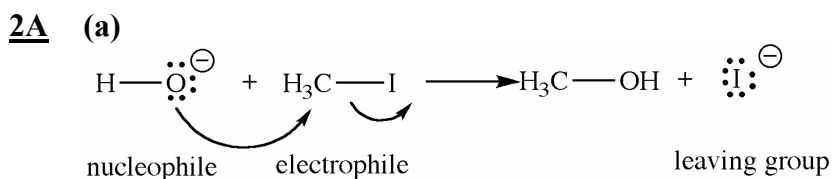


Chapter 27 Answers

Practice Examples

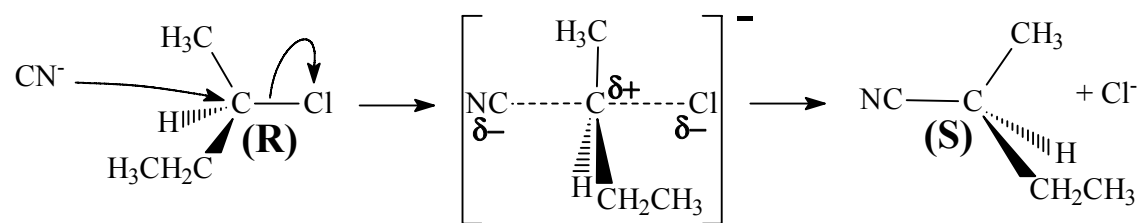
- 1A** (a) substitution
(b) rearrangement
(c) addition

- 1B** (a) elimination
(b) substitution
(c) substitution

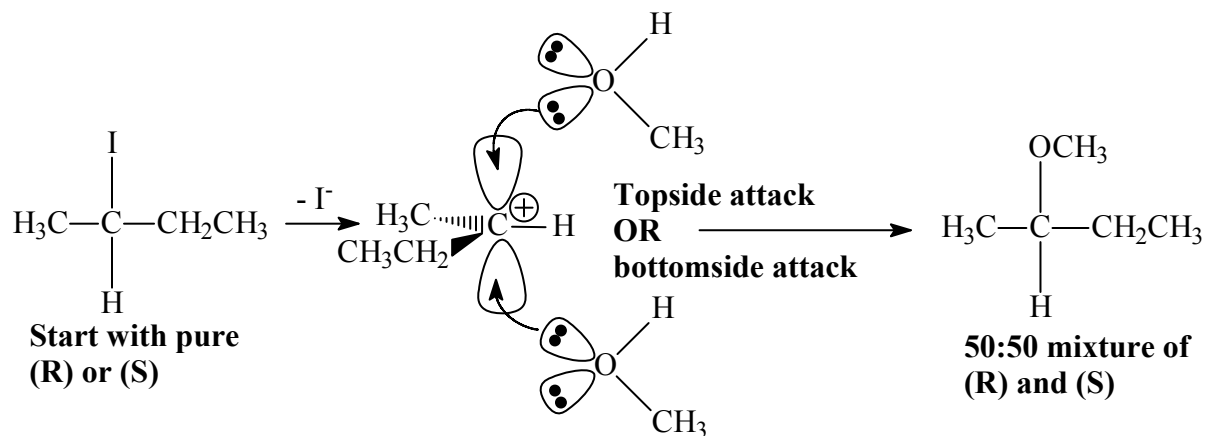


- 3A** (a) $\text{CH}_3\text{C}\equiv\text{C}^- + \text{CH}_3\text{Br} \xrightarrow{\text{S}_{\text{N}}2} \text{CH}_3\text{C}\equiv\text{CCH}_3 + \text{Br}^-$
 (b) no reaction is expected
 (c) $\text{CH}_3\text{NH}_2 + (\text{CH}_3)_3\text{CCl} \xrightarrow{\text{S}_{\text{N}}1} \text{CH}_3\text{NH}_2\text{C}^+(\text{CH}_3)_3 + \text{Cl}^-$

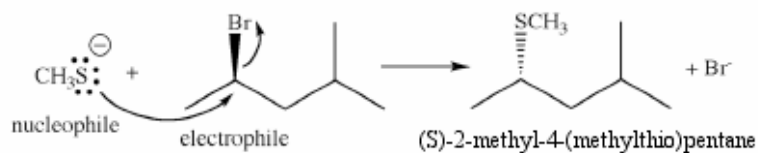
3B (a) S_N2 mechanism



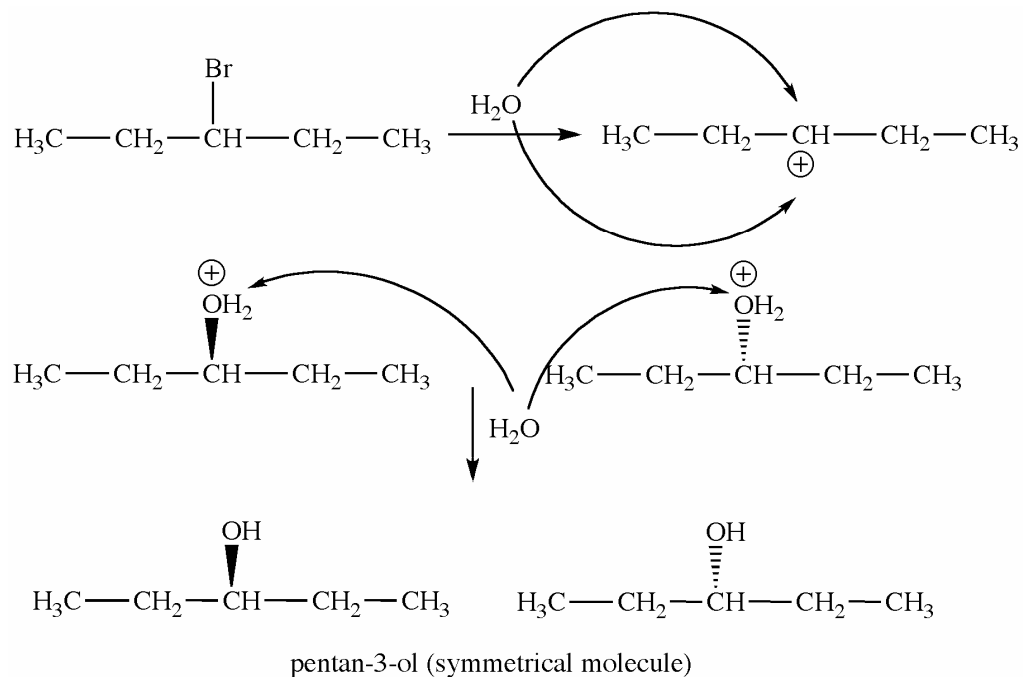
(b) S_N1 mechanism



4A S_N2 mechanism

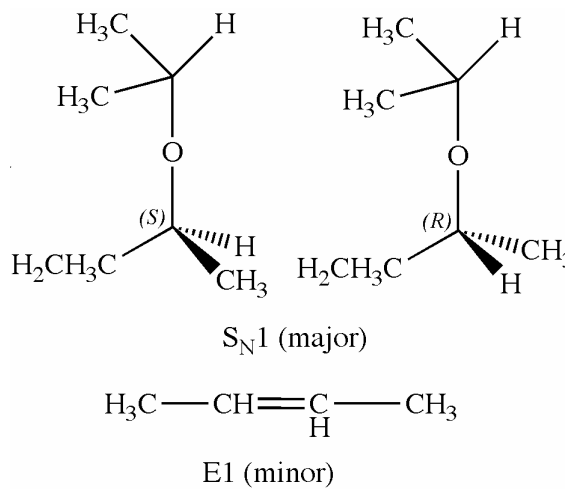


4B S_N1 mechanism

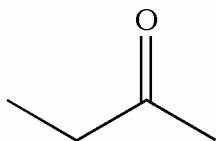


5A This is an S_N2 reaction leading to the alkyl sulfide product.

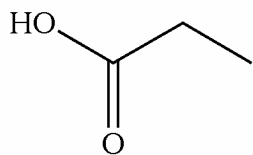
5B



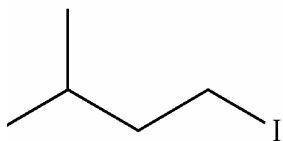
6A (a)



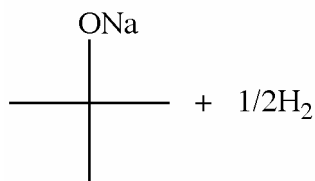
(b)



6B (a) The reactions proceed via a S_N2 mechanism.

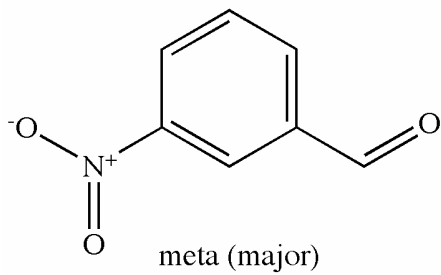


(b)

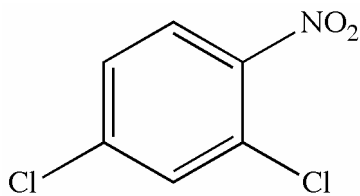


7A

3-nitro-benzaldehyde



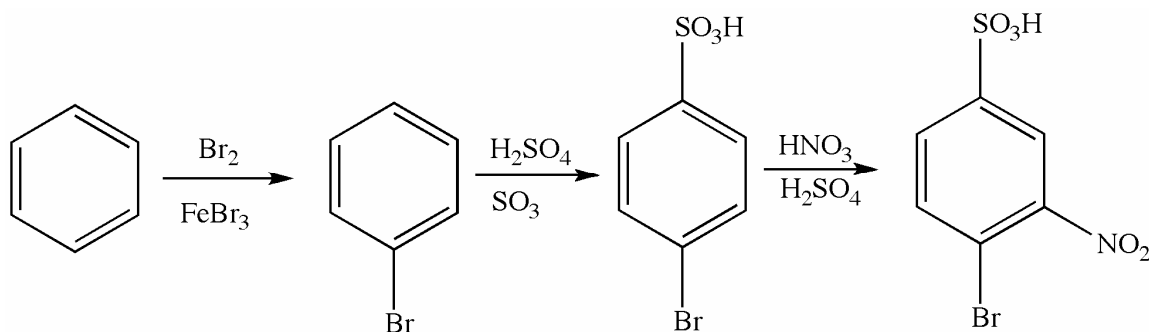
7B



Integrative Example

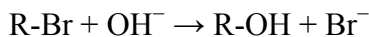
8A Alkanes are relatively unreactive. However, they will undergo bromination reaction in the presence of light. Such reaction will generate bromo-cyclohexane in the first step. In the presence of a base, elimination will occur resulting in the formation of cyclohexene. Subsequent repetition of these two steps will generate the desired product, 1,3-cyclohexadiene.

8B

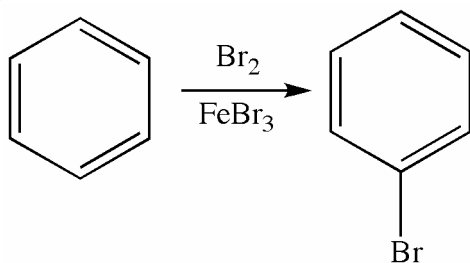


Exercises

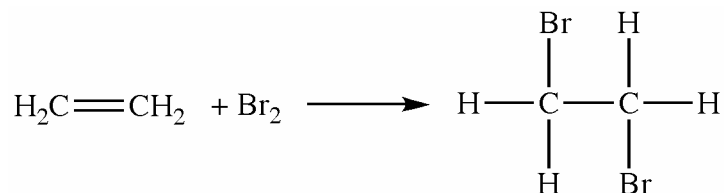
- 1.** (a) Nucleophilic substitution is a fundamental class of substitution reaction in which an "electron rich" nucleophile selectively bonds with or attacks the positive or partially positive charge of an atom attached to a group or atom called the leaving group; the positive or partially positive atom is referred to as an electrophile.



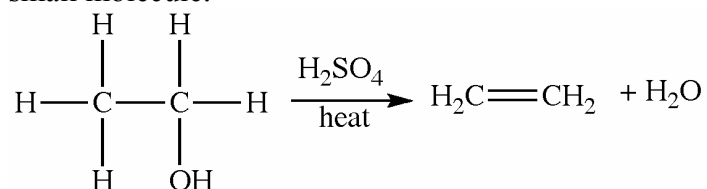
- (b) Electrophilic substitution reactions are chemical reactions in which an electrophile displaces another group,



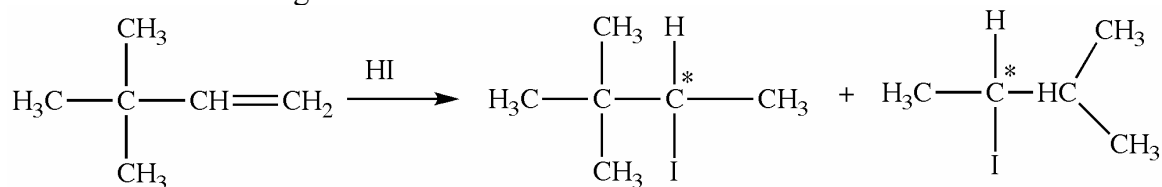
- (c) In an addition reaction, a molecule adds across a double or triple bond in another molecule.



(d) In an elimination reaction, atoms or groups that are bonded to adjacent atoms are eliminated as a small molecule.

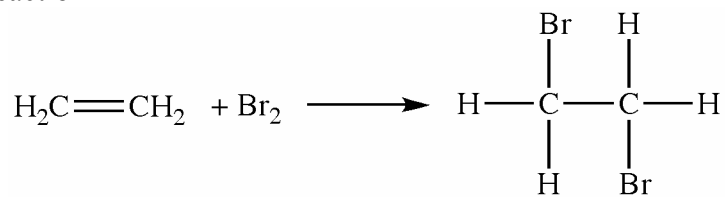


(e) When an organic compound undergoes a rearrangement reaction, the carbon skeleton of a molecule is rearranged.

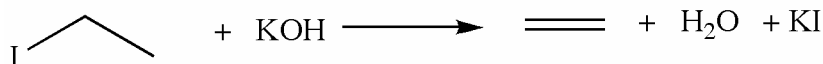


3. (a) substitution reaction (b) addition reaction (c) substitution reaction

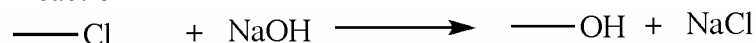
5. (a) addition reaction



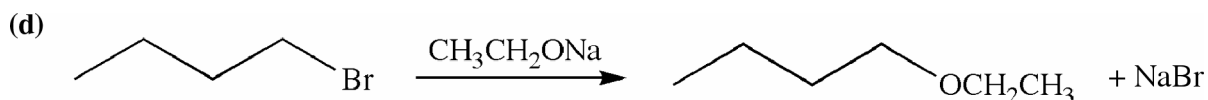
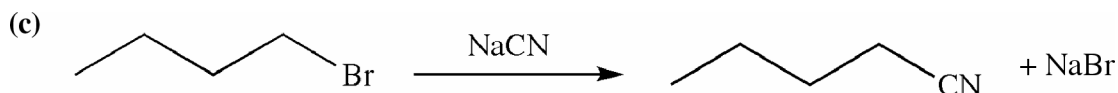
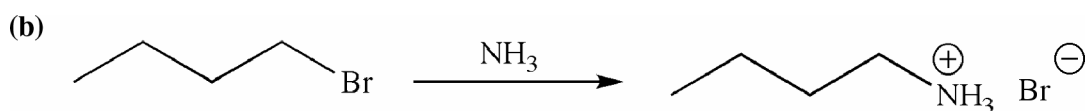
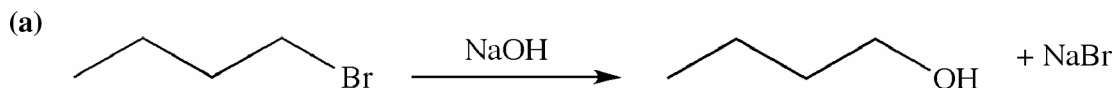
(b) elimination reaction



(c) substitution reaction

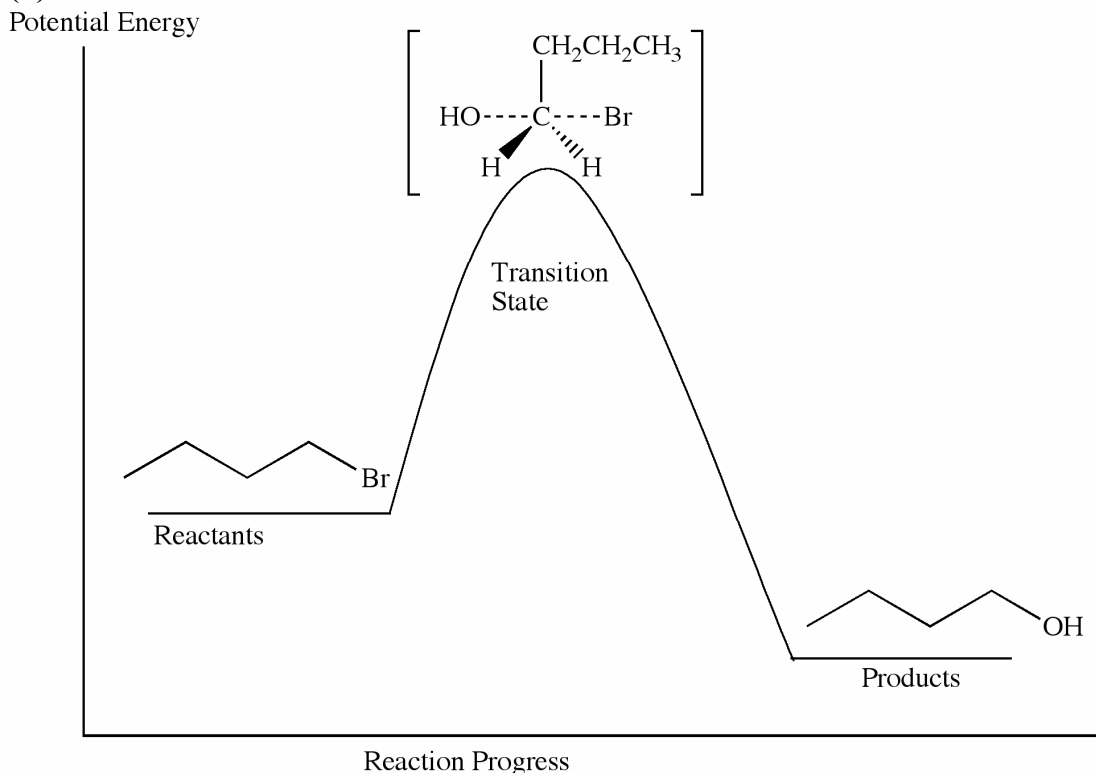


7.



9. (a) $\text{rate} = k[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}][\text{NaOH}]$

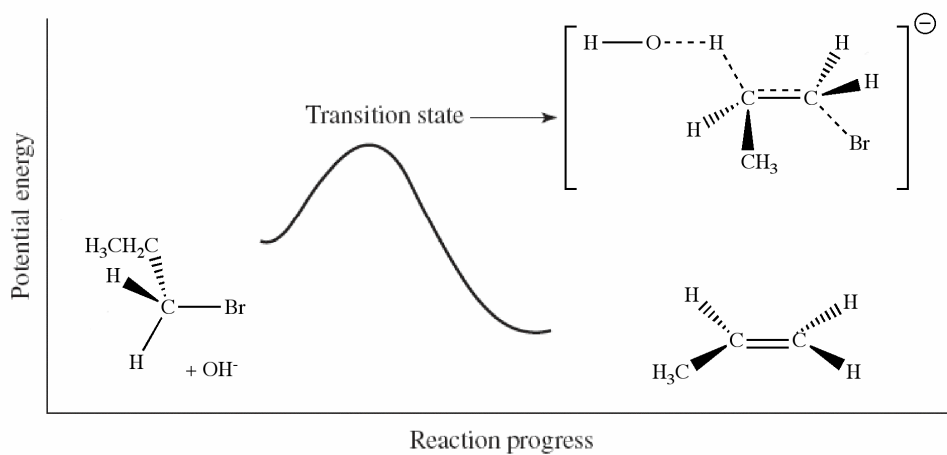
(b)



(c) Doubling the concentration of n-butyl bromide will also double the rate.

(d) Decreasing the concentration of NaOH by a factor of two will decrease the rate by a factor of 2.

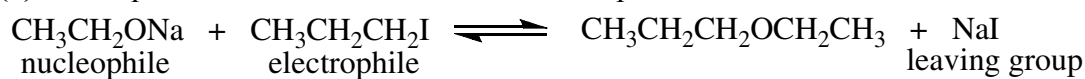
11.



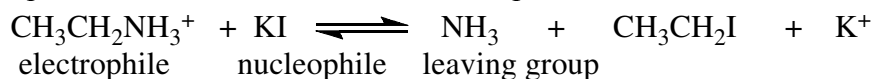
The rate will double.

The rate will decrease by a factor of 2.

- 13.** (a) The equilibrium favors the formation of the products.

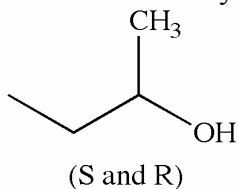


- (b) The equilibrium favors the formation of the products

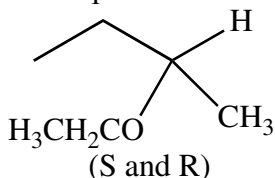


- 15.** Molecule (a) reacts faster in the $\text{S}_{\text{N}}2$ reaction than does molecule (b) because there is less steric hindrance. In molecule (b), the steric hindrance is associated with a methyl group being positioned in the axial position.

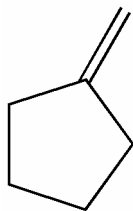
- 17.** The reaction most likely proceeded via an $\text{S}_{\text{N}}1$ mechanism.



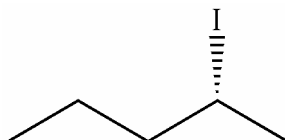
- 19.** The reaction proceeded via an $\text{S}_{\text{N}}1$ mechanism.



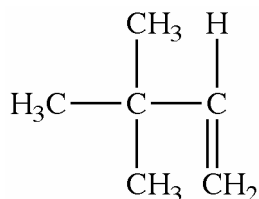
- 21.** (a) E_2 mechanism



- (b) $\text{S}_{\text{N}}2$ mechanism



- (c) E_2 mechanism



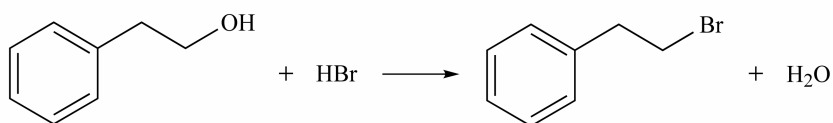
23. (a) $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$

(b) $(\text{CH}_3)_3\text{CO}^- \text{K}^+$

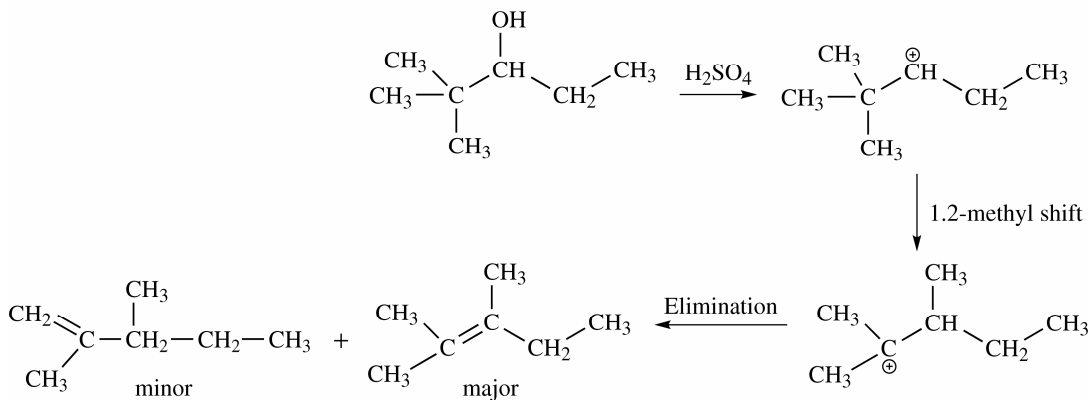
(c) $(\text{CH}_3)_2\text{CO}$

(d) There is no reaction.

25.



27. If no rearrangement occurs the expected product would be 4,4-dimethyl-pent-2-ene.

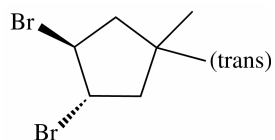


29. (a) $\text{CH}_3\text{—CH}_2\text{—CH}_3$

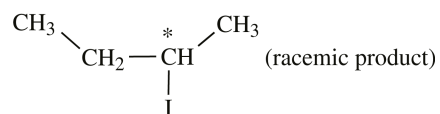
(b)

$$\begin{array}{c} \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \\ \text{E/Z} \\ \text{major} \\ + \\ \text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 \\ \text{minor} \end{array}$$

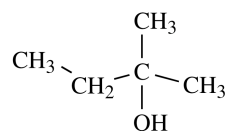
31. (a)



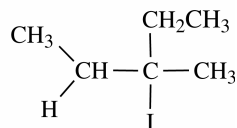
(b)



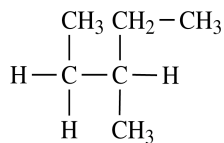
(c)



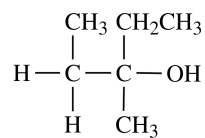
33. (a)



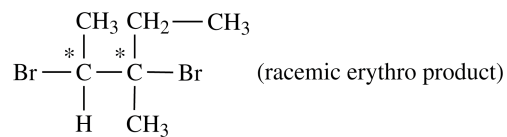
(b)



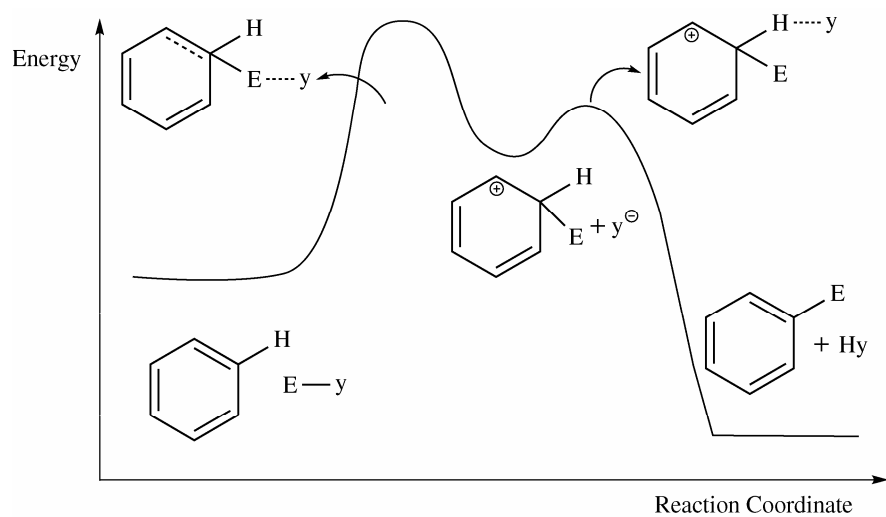
(c)



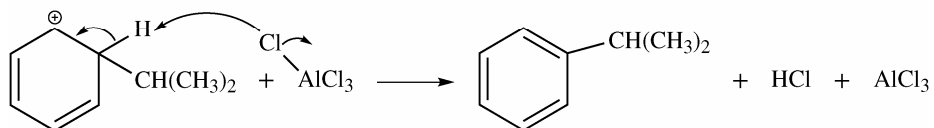
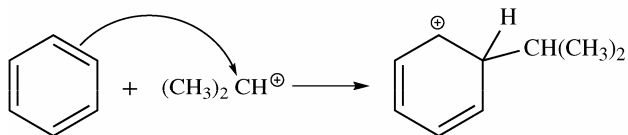
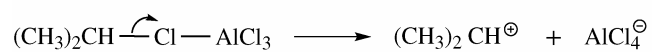
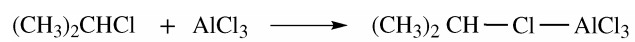
(d)



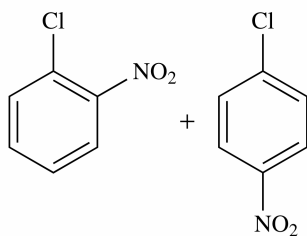
35.



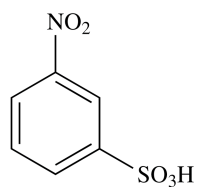
37.



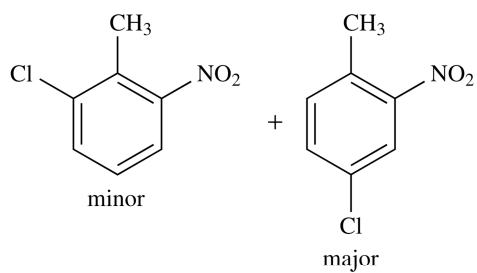
39. (a)



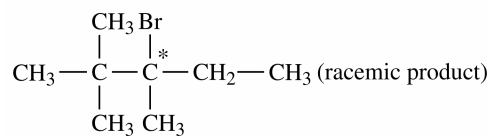
(b)

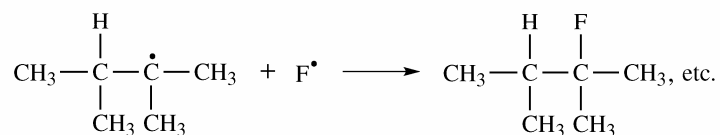
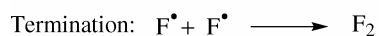
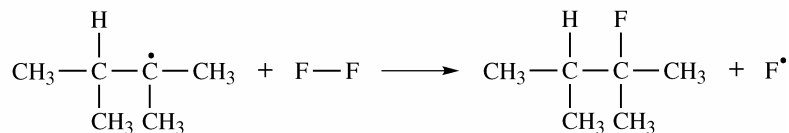
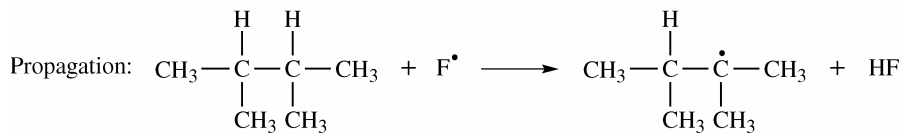
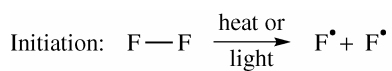


(c)



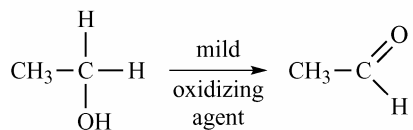
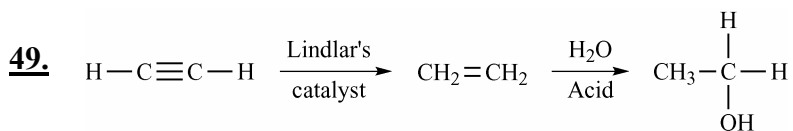
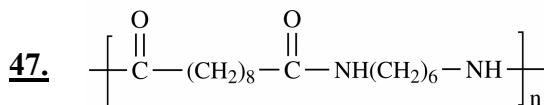
41.



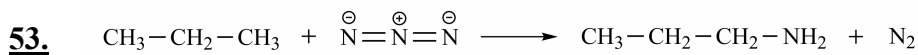
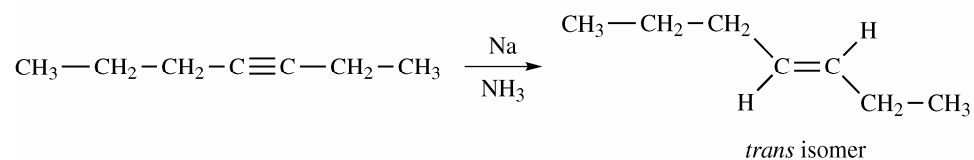
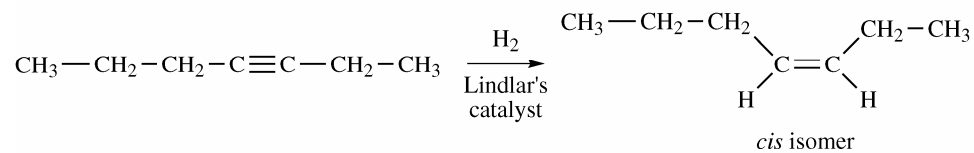
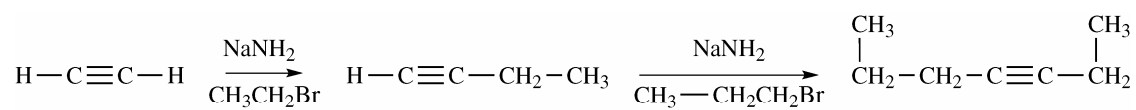
43. (a)

- (b)** Whereas the fluorine radical is so reactive, its attack on alkane is purely statistical. There are six times as many 1° hydrogens and 2° hydrogens in the reactant molecule.

- 45.** During the polymerization reaction, polymers of different chain-lengths are formed. As a result, we can only speak of average molecular weight.

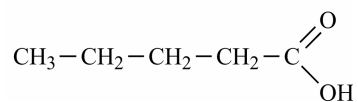


51.

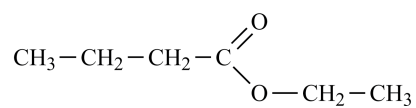


Integrative and Advanced Exercises

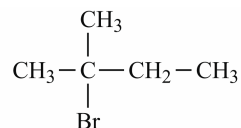
55. (a)

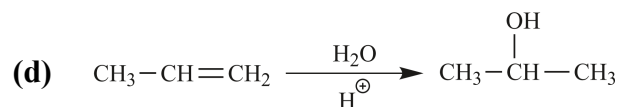
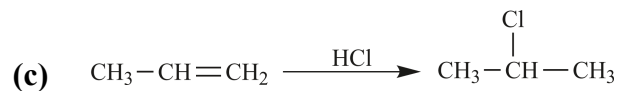
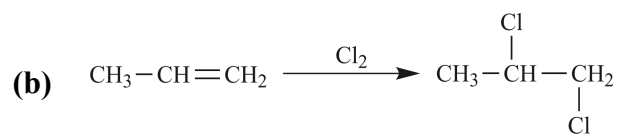
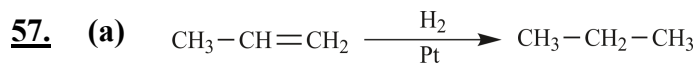


(b)



(c)

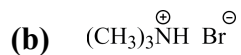




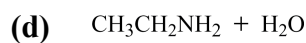
59. (a) Compound (3) reacts with dilute HCl.

(b) Compound (1) hydrolyzes.

(c) Compound (2) neutralizes dilute NaOH.

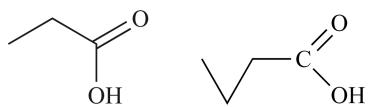


(c) no reaction

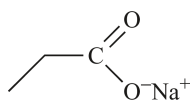


63. 2-butanol.

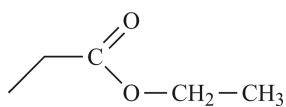
65. (a) Compound (1) and (3).



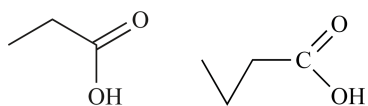
(b) Compound (2).



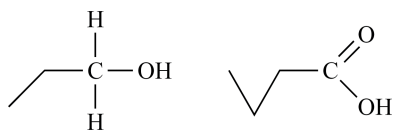
(c) Compound (2).



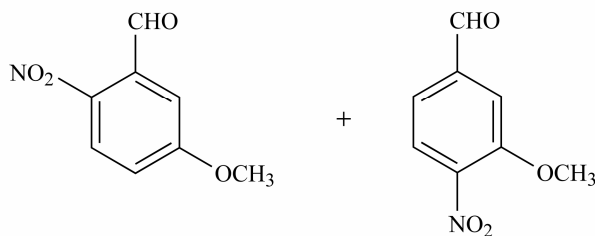
(d) Compound (1) and (3).



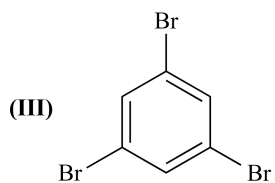
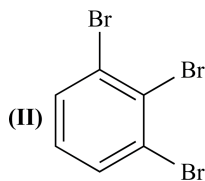
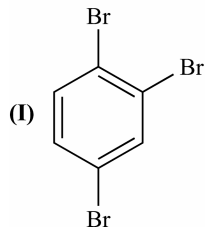
(e) Compound (2) and (3).



67.



69.



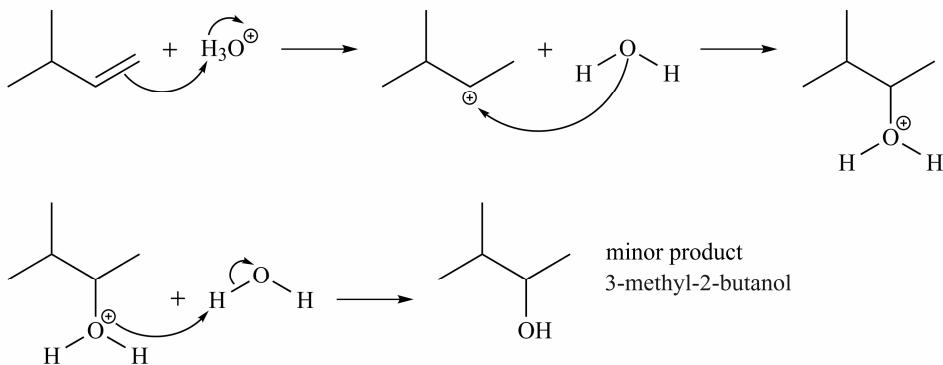
71.

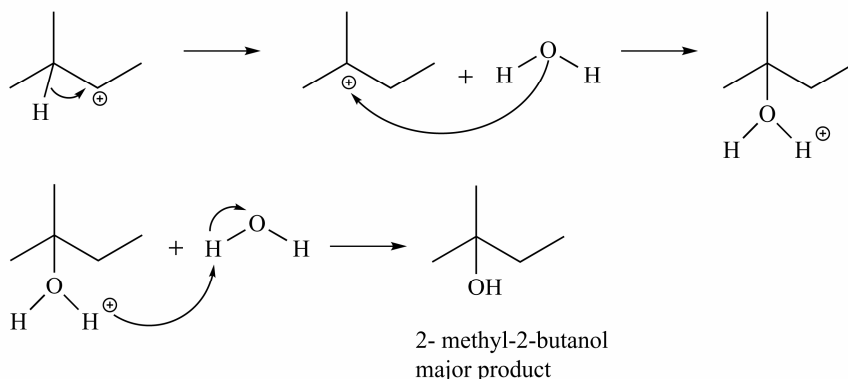
1-chloro-2-methylbutane	31%
1-chloro-3-methylbutane	16%
2-chloro-3-methylbutane	31%
2-chloro-2-methylbutane	21%

73.

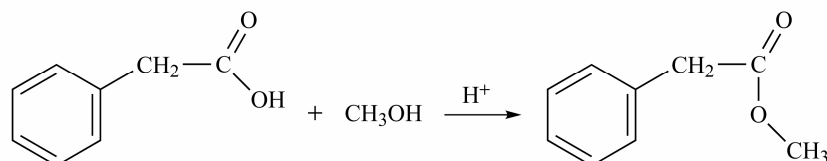
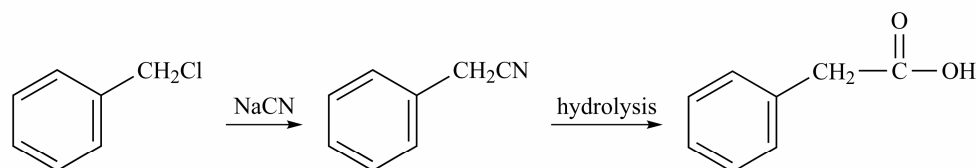
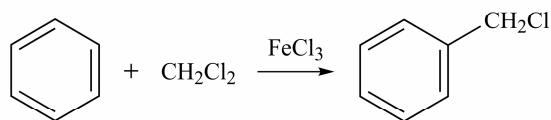
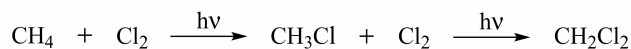
In the presence of strong acid (HI), the oxygen atom of the —OH group is protonated, forming $\text{CH}_3\text{CH}_2-\text{OH}_2^+$. H_2O is a weaker base than OH^- and is therefore a good leaving group.

75.





77.



Self-Assessment Exercises

79.

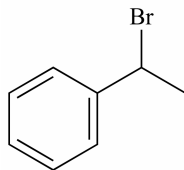
- Nucleophilic substitution corresponds to a substitution (either $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$) for aliphatic compounds. Electrophilic aromatic substitution is typical for aromatic compounds (an atom is replaced by an electrophile).
- An addition reaction is the opposite of an elimination reaction. In an addition reaction, two or more atoms (molecules) combine to form a larger one.
- $\text{S}_{\text{N}}1$ reaction involves the formation of carbocation. $\text{S}_{\text{N}}2$ reaction, on the other hand, is a one-step process in which bond breaking and bond making occur simultaneously at a carbon atom with a suitable leaving group.
- E1 reactions are unimolecular elimination reactions that proceed via carbocation intermediates. E2 reactions are bimolecular, one-step reactions that require an antiperiplanar conformation at the time of π -bond formation and β -bond breaking and do not involve carbocations.

81. (a) CN^-

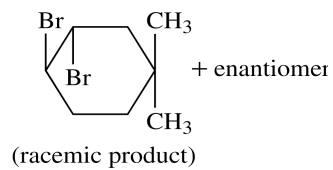
(b) CH_3I

83. Ether formation via the Williamson reaction proceeds via an $\text{S}_{\text{N}}2$ mechanism. As such, the isopropoxide/methyl iodide combination will be more ideal for $\text{S}_{\text{N}}2$ (uncrowded alkyl halide).

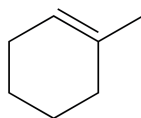
85. (a)



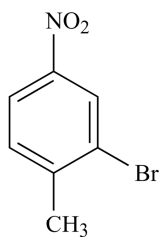
(b)



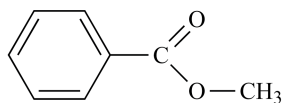
(c)



(d)



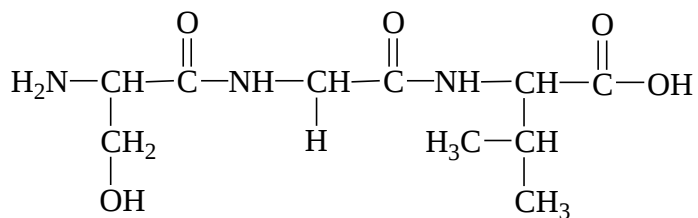
(e)



Chapter 28 Answers

Practice Examples

1a. dithreonylmethionine



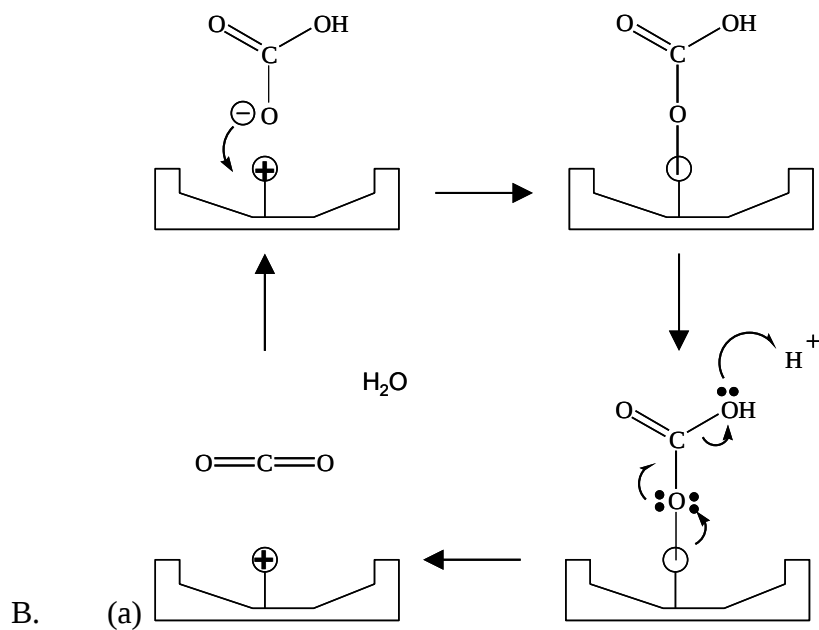
1b.

2a. Pentapeptide sequence: Gly-Cys-Val-Phe-Tyr.

2b. Hexapeptide sequence: Ser-Gly-Gly-Ala-Val-Trp.

Integrative Example

A. 0.300 m



B.

(a)

(b) $K_M = 0.01406 \text{ M}$, $k_2 = 4.8 \times 10^5 \text{ s}^{-1}$.

Exercises

1a. $3 \times 10^2 \text{ H}_3\text{O}^+$ ions

1b. $1.2 \times 10^5 \text{ K}^+$ ions

3. 5×10^6 protein molecules

5a. glyceryl palmitolinolenolaurate or glyceryl palmitoeleosterolaurate.

5b. glyceryl trioleate or triolein.

5c. myristate

7a. Both are triglycerides or glycerol esters. Trilaurin is saturated and a fat. Trinolein is unsaturated and an oil.

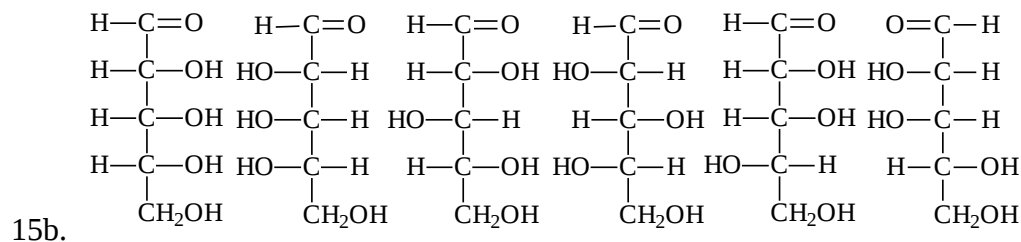
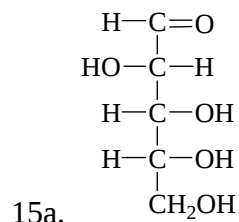
7b. Soaps are salts of fatty acids. Phospholipids are derived from glycerols, fatty acids, phosphoric acid, and a nitrogen containing base. Soaps and phospholipids have hydrophilic heads and hydrophobic tails.

9. Polyunsaturated fatty acids are characterized by a large number of $C = C$ double bonds in their hydrocarbon chain. Stearic acid has no $C = C$ double bonds and therefore is not unsaturated, let alone polyunsaturated. Eleostearic acid has three $C = C$ double bonds and thus is polyunsaturated. Polyunsaturated fatty acids are recommended in dietary programs since saturated fats are linked to a high incidence of heart disease. Of the lipids listed in Table 27-2, safflower oil has the highest percentage of unsaturated fatty acids.

11. $CH_2OHCHOHCH_2OH$ and $NaOOC(CH_2)_{14}CH_3$.

13a. L-Glucose, aldohexose.

13b. D-Erythrulose, ketotetrose.



17a. A dextrorotatory compound rotates the plane of polarized light to the right, namely clockwise.

17b. A levorotatory compound is one that rotates the plane of polarized light to the left, namely counterclockwise.

17c. A racemic mixture has equal amounts of an optically active compound and its enantiomer. Since these two compounds rotate polarized light by the same amount but in opposite directions, such a mixture does not exhibit a net rotation of the plane of polarized light.

17d. In organic nomenclature, this designation is given to a chiral carbon atom. The stereogenic center has an *R*-configuration if a curved arrow from the group of highest priority through to the one of lowest priority is drawn in a clockwise direction.

19. A reducing sugar has a sufficient amount of the straight-chain form present in equilibrium with its cyclic form such that the sugar will reduce $\text{Cu}^{2+}(\text{aq})$ to insoluble, red $\text{Cu}_2\text{O}(\text{s})$. Only free aldehyde groups are able to reduce the copper(II) ion down to copper (I). 0.397 g of Cu_2O should be produced.

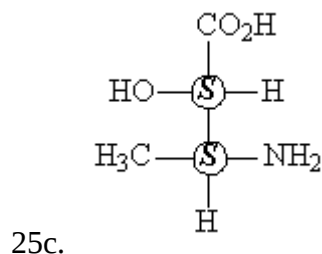
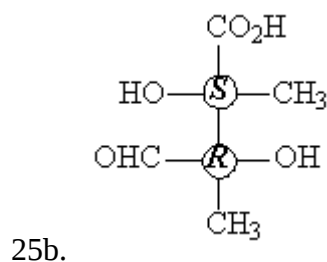
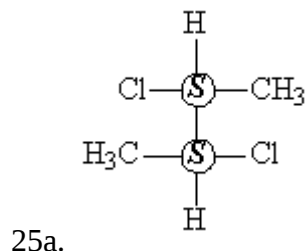
21. Diastereomers

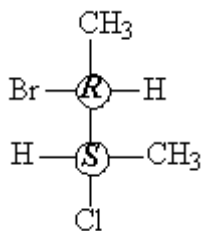
23a. Enantiomers: *S*-configuration (leftmost structure), *R*-config. (rightmost structure).

23b. Different molecules: different formulas

23c. Diastereomers: *S,R* configuration (leftmost structure—top to bottom), *S,S*-configuration (rightmost structure).

23d. Diastereomers: *R,R*-configuration (leftmost structure—top to bottom), *R, S*-configuration (rightmost structure—top to bottom).





25d.

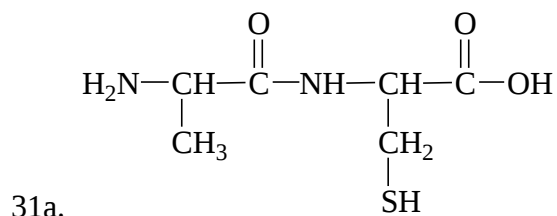
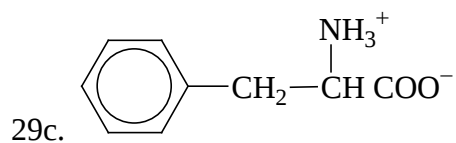
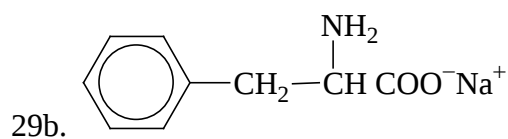
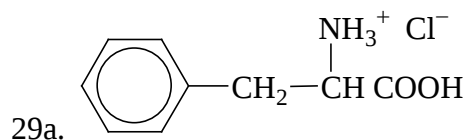
27a. An α -amino acid has an amine group (—NH_2) bonded to the same carbon as the carboxyl group (—COOH). For example, glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) is the simplest α -amino acid.

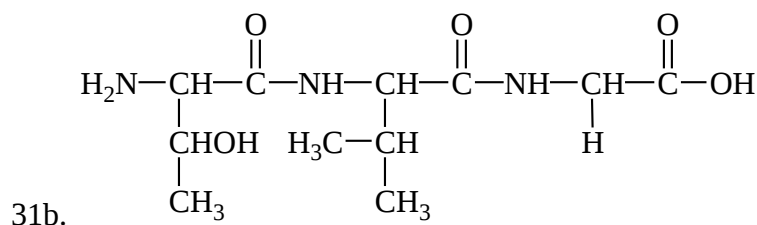
27b. A zwitterion is a form of an amino acid in which the amine group is protonated (—NH_3^+) and the carboxyl group is deprotonated (—COO^-). For instance, the zwitterion form of glycine is $^+\text{H}_3\text{NCH}_2\text{COO}^-$.

27c. The pH at which the zwitterion form of an amino acid predominates in solution is known as the isoelectric point. The isoelectric point of glycine is $\text{pI} = 6.03$.

27d. The peptide bond is the bond that forms between the carbonyl group of one amino acid and the amine group of another, with the elimination of a water molecule between them.

27e. Tertiary structure describes how a coiled protein chain further interacts with itself to wrap into a cluster through a combination of salt linkages, hydrogen bonding, and disulfide linkages, to name a few.





33. Proline will not migrate very effectively under these conditions. Lysine will migrate toward the negatively charged cathode. Aspartic acid will migrate toward the positively charged anode.



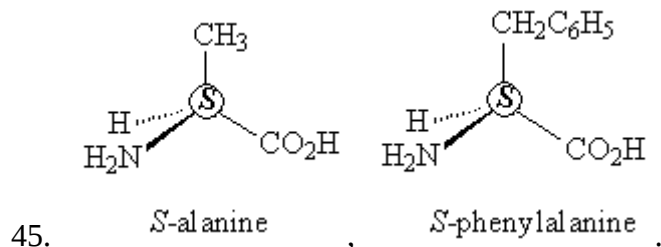
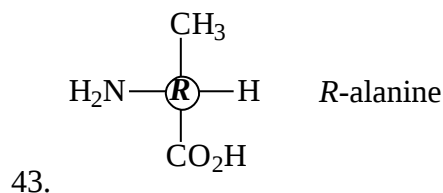
37a. There are 6 combinations: Lys-Ser-Ala, Lys-Ala-Ser, Ser-Lys-Ala, Ser-Ala-Lys, Ala-Ser-Lys, Ala-Lys-Ser.

37b. There are 6 combinations: Ala-Ser-Ala-Ser, Ala-Ala-Ser-Ser, Ala-Ser-Ser-Ala, Ser-Ser-Ala-Ala, Ser-Ala-Ser-Ala, Ser-Ala-Ala-Ser.

39a. Ala-Ser-Gly-Val-Thr-Leu.

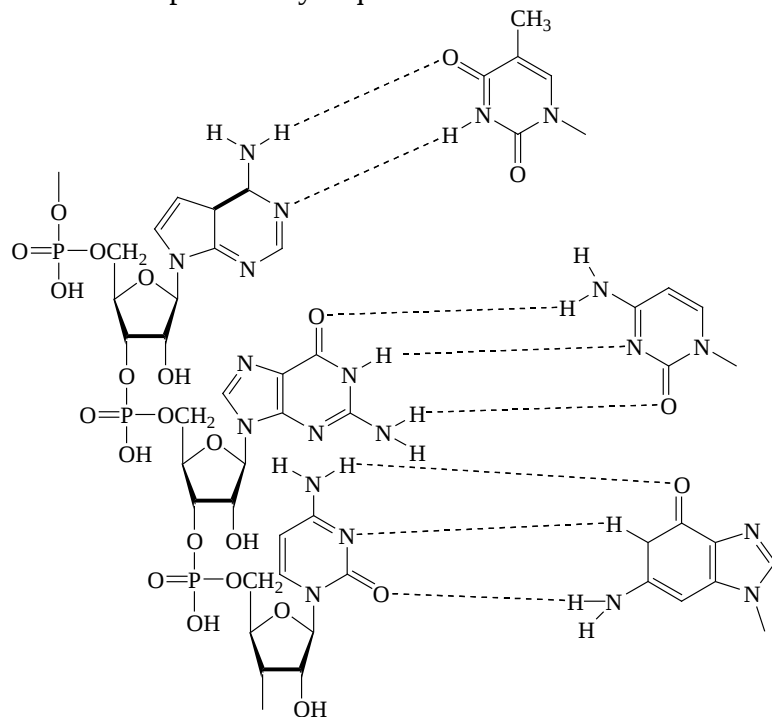
39b. alanyl-seryl-glycyl-valyl-threonyl-leucine, or alanylserylglycylvalylthreonylleucine.

41. The *primary* structure of an amino acid is the sequence of amino acids in the chain of the polypeptide. The *secondary* structure describes how the protein chain is folded, coiled, or convoluted. The *tertiary* structure of a protein refers to how different parts of the molecules interact with each other to maintain the overall shape of the protein macromolecule. Quaternary structure refers to how two or more protein molecules pack together into a larger protein complex. Not all proteins have a *quaternary* structure since many proteins have only one polypeptide chain.



47. Two major types of nucleic acids are DNA (deoxyribonucleic acid), and RNA (ribonucleic acid). Both of them contain phosphate groups. These phosphate groups alternate with sugars to form the backbone of the molecule. The sugars are deoxyribose in the case of DNA and ribose in the case of RNA. Attached to each sugar is a purine or a pyrimidine base. The purine bases are adenine and guanine. One pyrimidine base is cytosine. In the case of RNA the other pyrimidine base is uracil, while for DNA the other pyrimidine base is thymine.

49. The complementary sequence to AGC is TCG.



Integrative and Advanced Exercises

52. 2.9×10^3 g/mol. This is a minimum value because it is assumed that 1 Ag^+ ion is all that is necessary to denature each protein molecule.

56. 9.71

58. Nonapeptide: Arg-Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg.

59. One example for the required sequence would be AGA CCA CAA CGA. The redundancy enables the organism to produce a given amino acid in several ways in case of transcription error.

62. Met-Ser-Met-Met-Gly.

65a. 9.3×10^{-5}

65b. 1.8×10^5

65c. $\frac{[B]}{[A]} = 2.25$

Feature Problems

66a. Saponification value = 189. Iodine number = 86.0.

66b. Saponification value = 180. Iodine number = 81.6.

66c. The iodine number for safflower oil may range between 150 to 144. The saponification value may range between 211 and 179.

Self-Assessment Exercises

72. The answer is (b).

73. The answer is (d).

74. The answer is (a).

75. The answer is (d).

76. The answer is (e).

77. The answer is (c).

78. The answer is (b).

79. 129 g

80. RNA chain.

81. The answer is (e).

82. The answer is (b).

83. The answer is (a).

84. The answer is (d).

85. The answer is (c).

86. The answer is (d).

87. The answer is (b).

88. Gly-Cys-Val-Phe-Tyr.